

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES**

Applicant(s):	Yoshiaki Mori, et al.	Art Unit:	1756
Serial No.:	10/026,286	Examiner:	Daborah Chacko Davis
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Title:	Pattern Forming Method and Apparatus Used for Semiconductor Device, Electric Circuit, Display Module, and Light Emitting Device		

Brief on Appeal Under 37 CFR § 41.31

Sir:

INTRODUCTION

Pursuant to the provisions of 37 CFR § 41.31 *et seq.*, Appellants hereby appeal to the Board of Patent Appeals and Interferences (the "Board") from the Examiner's Final Rejection dated Oct. 18, 2006. A Notice of Appeal was timely filed with the requisite fee on March 15, 2007 in accordance with 37 CFR § 1.8. This Brief on Appeal is being filed in accordance with 37 CFR §41.37 and the Director is authorized to charge the requisite fees (37 CFR § 41.37 and 41.20(b)(2)) to the undersigned's Deposit Account No.: 19-2746.

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TABLE OF AUTHORITIES

N/A

REAL PARTY IN INTEREST

The parties listed in the caption of the brief have assigned all interest in the application from which the instant appeal is taken to:

Seiko Epson Corporation
4-1 Nishishinjuku 2-chome
Shinjuku-ku, Tokyo
Japan

Thus, Seiko Epson Corporation is the real party in interest.

RELATED APPEALS AND INTERFERENCES

There are no other appeals or interferences known to the Appellants, Appellants' legal representative, or assignee that will directly affect or be directly affected by or have a bearing on the Board's decision in the instant appeal.

STATUS OF CLAIMS

Claims 1-22 are under final rejection and are the subject of this appeal.

Claims 23-64 are withdrawn from consideration.

STATUS OF AMENDMENTS

No amendment has been filed subsequent to the final rejection.

SUMMARY OF CLAIMED SUBJECT MATTER

In the following, the format of the claims will be maintained to allow easy reference to the actual claim language. References to "Fig." numbers and reference characters are references to drawings of the subject application, and references to paragraph number, page number, and/or line numbers are references to the specification of the subject application.

Independent Claim 1

The present invention, as recited in independent Claim 1, is directed to a pattern forming method (Fig. 10, para. 185-188 and/or Figs. 18(1)-19(3) para. 220-334) characterized by:

forming a mask having pattern-forming openings on a workpiece surface (S130), and then supplying (S132) and solidifying (S133) an electrically

conductive liquid pattern material (para. 187) in the pattern-forming openings of the mask.

[Para. 0019] To achieve the above object, a pattern forming method according to the present invention is characterized by forming a mask having pattern forming openings on a workpiece surface, and then supplying and solidifying a liquid pattern material in the pattern forming openings of the mask. An organometallic compound solution or a solution of a powder of an inorganic material dissolved in solvent can be used as the liquid pattern material.

[Para. 00187] Next, a liquid pattern material 312 comprising an organometallic compound is supplied by a specific-volume discharge device such as the print head of an inkjet printer to the pattern forming openings in the mask processed for hydrophobic as described above. By heating the workpiece 20 to a specific temperature by means of a heater built in to the table on which the workpiece 20 is placed, supplying the liquid pattern material 312 to the openings and heating and solidifying the liquid pattern material are performed at the same time, and the pattern forming process ends with step S132.

Independent Claim 2

The present invention, as recited in independent Claim 2, is directed to a pattern forming method (Fig. 8, para. 175-178) characterized by:

a mask forming process (S110) for forming a mask having pattern-forming openings on a workpiece surface;

a pattern material supplying process (S112) for supplying a liquid-pattern material to the pattern-forming openings while also drying the liquid-pattern material (para. 117);

a process for removing the mask from the workpiece (S115); and

an annealing process for annealing dried solute of the liquid-pattern material (S116).

[Para. 00173] ... Moreover, because the liquid pattern material 312 is annealed in the pattern annealing process *after* drying in the pattern drying process in this first pattern forming method, the formation of internal voids and the *formation of deformation recesses in the formed pattern surface when the liquid pattern material 312 solidifies can be prevented*.

[Para. 00178] As in the first embodiment of a pattern forming method described above, a mask removal process (step S115) and pattern annealing process in step S116 are *applied in order*. These steps are also the same as in the previous embodiment.

[Para. 00277] ... if the carbonization temperature of the resist film is lower than the annealing temperature of the pattern film 660, *the resist film (mask 656) will carbonize during the annealing process* and removing the mask 656 will be difficult. In this case, *therefore, the mask removal process is performed first and then the pattern annealing process is*

performed. It should be noted that because the carbonization temperature of PMMA, a typical resist, is approximately 260°C, and the annealing temperature of an ITO film is 500°C or higher, the resist removal process is performed first and then the annealing process is performed.

Independent Claim 3

The present invention, as recited in independent Claim 3, is directed to a pattern forming method (Fig. 7, para. 162-174) comprising:

a mask forming process (S100) for forming a mask having pattern-forming openings on a workpiece surface;

[Para. 00162] ... this first pattern forming method first forms a mask having pattern forming openings on the surface of the workpiece. This mask forming step S100 is accomplished by the mask forming unit 100 shown in Fig. 1. More specifically, the workpiece 20 is conveyed into the mask material coating unit 110 shown in Fig. 2 of the mask forming unit 100. The photoresist 114 is then coated to and dried on the surface of the workpiece 20 by the mask material coating unit 110.

[Para. 00163] The workpiece 20 is then conveyed to the mask patterning unit 120. The mask material, that is, resist film, is then exposed in the exposure unit 122 of the mask patterning unit 120 and developed in the developer unit 124. A mask having pattern forming openings in the resist film is thus formed on the surface of the workpiece 20. It should be noted that the pattern forming openings could be written directly in the resist film using an electron beam or laser.

[Para. 00164] The surface of the mask is then processed for hydrophobic in the hydrophobic processing unit 200 (step S101). This mask hydrophobic process can be accomplished by generating active fluorine in the discharge unit 210 shown in Fig. 3 and supplying the active fluorine to the process chamber 218 in which the workpiece 20 is placed. It will also be noted that this workpiece surface hydrophobic process could be accomplished using an apparatus as shown in Fig. 6 to form a hydrophobic film such as a fluoropolymer film or silicon polymer film on the mask surface. When a hydrophobic process is applied according to the method shown in Fig. 3, the hydrophobic film present in the pattern forming openings is preferably removed or made hydrophilic using ultraviolet light, an electron beam, or laser, for example. Yet further, *if the mask is formed by a hydrophobic film by means of mask forming unit 150 as shown in Fig. 5 or Fig. 6, the hydrophobic mask processing step can be omitted as indicated by the dotted line in Fig. 7.*

a pattern material supplying process for supplying a liquid-pattern material to the pattern-forming openings (S102);

[Para. 00165] As shown in step S102, a pattern material supply step is executed to supply liquid pattern material 312 to the pattern forming openings in the mask. This pattern material supply step is accomplished by the pattern material supply unit 300 shown in Fig. 4. ...

[Para. 00167] It will be noted that supplying the liquid pattern material 312 to the pattern forming openings of the mask formed on the workpiece 20 can be done by spin coating the liquid pattern material 312, *or by*

using a specific-volume discharge device such as the print head of an inkjet printer.

[Para. 00169] Unnecessary pattern material can thus be easily removed by removing liquid pattern material 312 adhering to the mask surface at the stage at which the liquid pattern material is supplied to the pattern forming openings. *It is therefore possible to eliminate a step for removing solidified pattern material that is difficult to remove after the liquid pattern material is solidified in a drying process*, described below, and the mask can therefore be easily removed. *Note that when the liquid pattern material is supplied directly to the pattern forming openings by the above-noted specific-volume discharge device, the adherent liquid removal step of step S103 can be omitted.*

a drying process for evaporating solvent in the liquid-pattern material (S104);

[Para. 00170] The liquid pattern material 312 supplied to the pattern forming openings is then dried (step S104). *Evaporating solvent contained in the liquid pattern material 312 is the main objective of drying the liquid pattern material 312*, and is normally achieved by heating the workpiece 20 to 80° to 120° C. ...

a mask removal process for removing the mask from the workpiece (S105); and

[Para. 00171] A mask removal step is performed next (step S105). This mask removal step can be accomplished by immersing the workpiece 20 in a solution able to dissolve the resist film similarly to a conventional semiconductor device manufacturing process....Yet further, the mask removal step could be accomplished by ashing

an annealing process for annealing dried solute in the liquid-pattern material (S106).

[Para. 00172] After removing the mask, solute contained in the liquid pattern material supplied to the pattern forming openings is annealed in the pattern material setting unit 500 shown in Fig. 1 to complete the solute solidification process (step S106). This pattern annealing step is normally conducted by heating the workpiece 20 to a higher temperature, such as 150°C or higher, than used in the pattern drying process.

[Para. 00173] It is thus possible to form a specifically detailed pattern on the surface of the workpiece 20. Moreover, *because the liquid pattern material 312 is annealed in the pattern annealing process after drying in the pattern drying process in this first pattern forming method, the formation of internal voids and the formation of deformation recesses in the formed pattern surface when the liquid pattern material 312 solidifies can be prevented.*

Independent Claim 4

The present invention, as further recited in independent Claim 4, is directed toward a pattern forming method (Fig. 12, [00195] - [00198]) comprising:

a mask forming process (S150) for forming a mask having pattern-forming openings on a workpiece surface;

a pattern material supplying process (S152) for supplying an electrically conductive liquid-pattern material to the pattern-forming openings;

[Para. 00195] Fig. 12 is a flow chart of a sixth pattern forming method according to the present invention. This pattern forming method sequentially performs the mask forming process (step S150), mask hydrophobic process (step S151), and pattern material supply process (step S152) using the same methods as in the above described embodiments.

[Para. 00187] ... a liquid pattern material 312 comprising an organometallic compound is supplied by a specific-volume discharge device such as the print head of an inkjet printer to the pattern forming openings...

a solidifying process (S153 and S154) for solidifying the liquid-pattern material supplied into the pattern-forming openings; and

a mask removal process (S155) for removing the mask from the workpiece after sequentially performing plural times the pattern material supply process and solidifying process.

[Para. 00196] The liquid pattern material 312 supplied to the pattern forming openings is then dried and annealed as the heating and solidifying process (steps S153, S154). When this annealing process is completed, the process returns to step S152 to complete a second pattern material supply process, and the drying process and annealing process of steps S153 and S154 are then executed. These steps S152 to S154 are repeated as many times as necessary. When the last pattern annealing process is completed, the mask is removed as described above (step S155).

Independent Claim 5

Another aspect of the present invention, as recited in independent Claim 5, is directed to a pattern forming method (Fig. 17, para. 216-219) characterized by:

a mask forming process for forming a mask having pattern-forming openings on a workpiece surface (S200);

a pattern material supplying process for supplying a liquid-pattern material to the pattern-forming openings (S202);

an adherent-liquid removal process for removing liquid pattern material that adhered to the mask surface when the liquid-pattern material was supplied to the openings (S203);

a drying process for drying by evaporating solvent from the liquid-pattern material in the pattern-forming openings (S204);

an annealing process for annealing the dried solute after sequentially performing plural times the pattern material supply process, adherent-liquid removal process, and drying process (S205); and

[Para. 00219] ... steps S204 to S206 can be performed after repeating the pattern material supply process of step S202 and the adherent liquid removal process of step S203 the necessary number of times...

a mask removal process for removing the mask from the workpiece (S206).

Independent Claim 6

Another aspect of the present invention, as recited in claim 6, is directed to a pattern forming method (Fig. 7, and/or Fig. 9, and/or Fig. 15, para. 210-212) characterized by:

a mask forming process for forming a mask having pattern-forming openings on a workpiece surface (S180);

a pattern material supplying process for supplying a liquid-pattern material to the pattern-forming openings (S181);

a drying process for drying by evaporating solvents from the liquid-pattern material in the pattern-forming openings (S182); and

an annealing process for annealing the dried solute after sequentially performing plural times the pattern material supply process and drying process (S182).

[Para. 00210] Fig. 15 is a flow chart of a ninth pattern forming method according to the present invention. This ninth pattern forming method first hydrophobes the surface of the workpiece 20 *in which pattern forming recesses are also formed* (step S180). Then using a discharge device such as the print head of an inkjet printer, a specific amount of liquid pattern material 312 is selectively supplied to the pattern forming recesses of the workpiece 20 (step S181). The liquid pattern material 312 is then heated and solidified (step S182) to complete pattern forming. Heating and solidifying the pattern material can be done at a relatively low temperature of 120°C or less as described above, or at a

higher temperature. *Pattern heating and solidifying can also contain a process for drying the liquid pattern material and a subsequent annealing process.*

Independent Claim 7

A further aspect of the present invention, as recited in independent claim 7, is directed to a pattern forming method (Fig. 11, para. 189-194) characterized by:

a mask forming process for forming a mask having pattern-forming openings on a workpiece surface (S140);

a pattern material supplying process for supplying an electrically conductive liquid-pattern material to the pattern-forming openings (S142);

a solidifying process for solidifying the liquid-pattern material supplied into the pattern-forming openings (S143);

[Para. 00191] ... When the first pattern material supply process is completed, the pattern material drying process is applied to evaporate the solvent in the liquid pattern material (step S143).

a solid-material removal process for removing solidified elements of the liquid-pattern material that adhered to the mask surface when the liquid-pattern material was supplied to the pattern-forming openings (S144); and

[Para. 00192] Dried solids of the liquid pattern material 312 adhering to the mask surface are then removed as shown by step S144. The dried solids can also be removed as described above. Once the dried solids are removed, the process returns to step S142 and steps S142 to S144 are repeated the required number of times....

a mask removal process for removing the mask from the workpiece after sequentially performing plural times the pattern material supply process, solidifying process, and solid-material removal process (S146).

Independent Claim 8

The present invention, as recited in independent claim 8, is further directed to a pattern forming method (Fig. 11, para. 189-194) characterized by:

a mask forming process for forming a mask having pattern-forming openings on a workpiece surface (S140);

a pattern material supplying process for supplying a liquid-pattern material to the mask openings (S142);

a drying process for drying by evaporating solvent from the liquid-pattern material in the pattern-forming openings (S143);

a solid-material removal process for removing dried solids of the liquid-pattern material that adhered to the mask surface when the liquid-pattern material was supplied to the pattern-forming openings (S144);

an annealing process for annealing the dried solute after sequentially performing plural times the pattern material supply process, drying process, solid-material removal process (S145); and

a mask removal process for removing the mask from the workpiece (S146).

Independent Claim 9

The present invention, as recited in independent claim 9, is further directed to a pattern forming method (Fig. 16, para. 213-216) characterized by:

a mask forming process for forming a mask having pattern-forming openings on a workpiece surface (S190);

[Para. 00213]: Fig. 16 is a flow chart of a tenth pattern forming method according to the present invention. As described above, the pattern forming method of this embodiment first hydrophobic processes the surface of the workpiece 20 *in which pattern forming recesses are also formed* (step S190)

a pattern material supplying process for supplying a liquid-pattern material to the mask openings (S191);

a drying process for drying by evaporating solvent from the liquid-pattern material in the pattern-forming openings (S192);

a solid-material removal process for removing dried solids of the liquid-pattern material that adhered to the mask surface when the liquid-pattern material was supplied to the pattern-forming openings (S193);

[Para. 00214] ... dried solids of the liquid pattern material 312 adhering to the workpiece surface are removed by CMP, plasma etching at atmospheric pressure, or other technique (step S193). ...

an annealing process for annealing the dried solute (S194); and
a mask removal process for removing the mask from the workpiece after sequentially performing plural times the pattern material supply process, drying process, solid-material removal process, and annealing process (S193a).

[Para. 00215] It should be noted that as indicated by the dotted line in Fig. 16, the second and subsequent pattern material supply processes can be performed after the dried solid removal process of step S193, or after the pattern material annealing process of step S194. ...

Dependent Claim 10

Dependent Claim 10, which depends from claim 1, recites:

wherein the mask has hydrophobic properties on at least the surface thereof for repelling the liquid pattern material (Fig. 1, 200).

[Para 132] ... Fig. 1 is a schematic block diagram of a pattern forming apparatus according to a first embodiment of the present invention. As shown in Fig. 1, this pattern forming apparatus 10 has a mask forming unit 100 for forming a mask on a surface of a semiconductor substrate or other workpiece, *hydrophobic processing unit 200 for making the mask surface hydrophobic*, and pattern material supply unit 300 for supplying a liquid pattern material to a pattern forming opening disposed in the mask formed by the mask forming unit 100.

Dependent Claim 11

Dependent Claim 11, which depends from claim 1, recites:

wherein the mask is hydrophobic for repelling the liquid pattern material.

[0037] At least the surface of the mask is preferably hydrophobic. If the workpiece is then rotated, for example, *when supplying the liquid pattern material to the pattern forming openings in the mask, liquid pattern material on the workpiece surface will move easily over the workpiece surface and into the openings*, and the liquid pattern material can thus be supplied easily, quickly, and evenly into the pattern forming openings. *Material adhering to the mask surface can also be easily removed because the mask surface is hydrophobic.*

[00141] ... workpiece 20 itself is not made hydrophobic. ...

[00143] As shown in Fig. 4, the pattern material supply unit 300 has an atomizer 311 for atomizing the liquid pattern material, and a shower head 310 for misting the liquid pattern material 312 atomized by the atomizer 311....

[00144] A liquid pattern material source 314 and mist gas source 316 are connected to the atomizer 311. *The liquid pattern material source 314 supplies an organometallic solution or other liquid pattern material 312 to the atomizer 311. ...*

[00145] A process stage 318 with a workpiece 20 having a mask on the surface thereof placed on the process stage 318 is disposed below the shower head 310. The process stage 318 is mounted on the rotating shaft 322 of a motor 320, that is, a rotating means, and rotates freely in the direction of arrow 324. By thus rotating the process stage 318, *the pattern material supply unit 300 of this embodiment can easily supply liquid pattern material 312 to the pattern forming openings in the mask*, and unneeded liquid pattern material 312 adhering to the mask surface can be removed.

[00149] It should be noted that the adherent liquid removal means could be the motor 320. More specifically, liquid pattern material 312 adhering to the mask surface can be removed by centrifugal force by increasing the speed of the motor 320. The adherent liquid removal means could also be comprised with a cylinder, for example, for tilting the base, not shown in the figures, on which the motor 320 and process stage 318 are disposed to incline the workpiece 20 by way of the intervening base *so that the liquid pattern material 312 adhering to the hydrophobic treated surface of the mask rolls off.*

[00150] ... The pattern material supply unit 300 could also be comprised to drip the liquid pattern material onto the rotating workpiece 20 to deposit the pattern material into the pattern forming openings by spin coating.

Dependent Claim 12

Dependent Claim 12, which depends from claim 1, recites:

wherein the liquid-pattern material is solidified by applying heat.

Para. 0040: Heating and solidifying the liquid pattern material can as necessary comprise a drying process and an annealing process. This makes it possible to avoid producing voids in the pattern or deforming the pattern shape, and can achieve a detailed pattern with low internal stress. It will be noted, however, that the annealing process is not required if sufficient *solidification* is possible at a drying temperature of, for example, 80° to 120°C. Yet further, the drying process can be omitted if the process can start at a high temperature without causing any problems.

[Para. 0046] By supplying the liquid pattern material to pattern forming openings in the mask, and *drying and annealing it to solidify*, the present invention thus comprised can easily form a pattern without using vacuum equipment....

[Para. 0069] ... the liquid pattern material can be solidified by heating. If the liquid pattern material is solidified by heating, chemicals and expensive equipment are not needed ... Heat solidification of the liquid pattern material can comprise a drying process for evaporating solvent in the liquid pattern material, and an annealing process for annealing the solute. The occurrence of voids can be prevented, and a detailed pattern

with low internal stress and good shape precision can be formed, by thus annealing after drying the liquid pattern material.

[Para. 0090] The solidification unit comprises a heating means disposed in the pattern material supply unit for heating and solidifying the liquid pattern material.

[Para. 00152] The pattern material setting unit 500 can be comprised as a heating chamber or as a tunnel oven... *for heating and solidifying the liquid pattern material 312* in the pattern forming openings. The pattern material setting unit 500 could also be configured to solidify the liquid pattern material 312 using an infrared heater or laser beam or electron beam emissions. ...

[Para. 00172] ... solute contained in the liquid pattern material supplied to the pattern forming openings is annealed in the pattern material setting unit 500 shown in Fig. 1 to complete the *solute solidification process* (step S106).

Dependent Claim 13

Dependent Claim 13, which depends from claim 12, recites:

wherein heating and solidifying the liquid-pattern material comprises a drying process for evaporating solvent in the liquid pattern material, and an annealing process for annealing the dried solute.

[0040] Heating and solidifying the liquid pattern material can as necessary comprise a drying process and an annealing process.

[00170 - 00172] The liquid pattern material 312 supplied to the pattern forming openings is then dried (step S104). Evaporating solvent contained in the liquid pattern material 312 is the main objective of drying the liquid pattern material 312, ... A mask removal step is performed next (step S105). ... After removing the mask, solute contained in the liquid pattern material supplied to the pattern forming openings is annealed in the pattern material setting unit 500 shown in Fig. 1 to complete the solute solidification process (step S106). This pattern annealing step is normally conducted by heating the workpiece 20 to a higher temperature, such as 150°C or higher, than used in the pattern drying process.

[00191 - 00192] Next, liquid pattern material 312 is supplied to the pattern forming openings of the mask as described above in the pattern material supply process of step S142. ... When the first pattern material supply process is completed, the pattern material drying process is applied to evaporate the solvent in the liquid pattern material (step S143). ... Once the last pattern material supply process, pattern material drying process, and dried solid removal process are completed, processing moves to the pattern annealing process shown in the next step S145 to anneal solutes contained in the liquid pattern material 312, complete the solidification reaction, and remove the mask as described above (step S146).

[Para. 00180] The pattern drying process of step S123, which is a pattern material heating and solidification process, and the pattern annealing process (anneal process) of step S124, are then performed. The pattern material drying process heats the workpiece 20 to 80° to 120°C, for example, *to vaporize solvent in the liquid pattern material* supplied to the

pattern forming openings. The pattern annealing process normally uses a temperature above that of the drying process, heating the workpiece 20 to a temperature, such as 150° to 220°C, that will not carbonize a mask made from a resist film, heating solute contained in the liquid pattern material 312 to a higher temperature *and completing the solidification reaction*. The drying and annealing processes can be accomplished by the heater 326 shown in Fig. 4, or by introduction to the special pattern material setting unit 500 shown in Fig. 1. To prevent oxidation of the pattern material, the drying and annealing processes are preferably accomplished in an inert atmosphere such as nitrogen.

Dependent Claim 14

Dependent Claim 14, which depends from claim 1, recites:

wherein the mask is removed from the workpiece after solidifying the liquid pattern material. (See Fig. 9, for example)

Dependent Claim 15

Dependent Claim 15, which depends from claim 1, recites:

wherein the liquid-pattern material is solidified after removing liquid-pattern material that adhered to the mask surface when the liquid-pattern material was supplied to the pattern-forming openings. (see Figs. 7, 13, 14, and 17, for example)

[00168 - 00171] Once the liquid pattern material 312 is supplied to the pattern forming openings, compressed air is discharged from the air knife 330 in an adherent liquid removal step for *removing the liquid pattern material adhering to the mask surface* (step S103). However, this adherent liquid removal step could alternatively be accomplished by spinning the workpiece 20 at high speed by means of the motor 320 shown in Fig. 4 to remove the liquid pattern material 312 adhering to the mask surface by means of centrifugal force, or by tilting the workpiece 20. Yet further, the adherent liquid removal step could be accomplished by operating the air knife 330 while spinning the workpiece 20 or inclining the workpiece 20.

[00169] Unnecessary pattern material can thus be easily removed by removing liquid pattern material 312 adhering to the mask surface at the stage *at which the liquid pattern material is supplied to the pattern forming openings*. It is therefore possible to eliminate a step for removing solidified pattern material that is difficult to remove after the liquid pattern material is solidified in a drying process, described below, and the mask can therefore be easily removed. Note that when the liquid pattern material is supplied directly to the pattern forming openings by the above-noted specific-volume discharge device, the adherent liquid removal step of step S103 can be omitted.

[00170] The liquid pattern material 312 supplied to the pattern forming openings is then dried (step S104). Evaporating solvent contained in the liquid pattern material 312 is the main objective of drying the liquid pattern material 312, and is normally achieved by heating the workpiece 20 to 80° to 120° C. The workpiece drying process can be accomplished using the heater 326 built in to the process table 318 shown in Fig. 4, or with a tunnel oven, infrared heater, or laser, not shown in the figures. The pattern material drying step is also preferably performed in an inert atmosphere, such as a nitrogen atmosphere, to prevent pattern oxidation. Of course, the drying step could be performed in an oxidizing atmosphere if oxidizing the pattern is not a problem or if oxidation is preferable.

[00171] A mask removal step is performed next (step S105). This mask removal step can be accomplished by immersing the workpiece 20 in a solution able to dissolve the resist film similarly to a conventional semiconductor device manufacturing process. The mask removal step can alternatively be accomplished immersing the workpiece 20 in ozonated water or other functional solution, or by ashing a mask made from a resist film using a supercritical fluid. Moreover, the mask removal step could drip a resist removal fluid onto the spinning workpiece 20 while the workpiece 20 is rotated as in a spin etching process. Yet further, the mask removal step could be accomplished by ashing with active oxygen generated by emitting an ultraviolet beam or electron beam into oxygen or ozone, or by an electrical discharge into oxygen or ozone at atmospheric pressure.

Dependent Claim 16

Dependent Claim 16 (Fig. 7), which depends from claim 6, recites:

wherein the annealing process (S106) is performed after removing the mask from the workpiece (S105).

Dependent Claim 17

Dependent Claim 17 (Fig. 9), which depends from claim 6, recites:

wherein the mask is removed from the workpiece (S125) after the annealing process (S124).

Dependent Claim 18

Dependent Claim 18 (Fig. 10), which depends from claim 2, recites:

wherein the process for removing the mask and the annealing process are performed simultaneously (In step S133, the mask removal process as well as the heating and solidifying process are combined).

[0044] ... removing the mask and annealing the solute can be accomplished simultaneously by forming the mask from a material with a high breakdown temperature.

Independent Claim 19

The present invention, as recited in independent claim 19, is further directed to a pattern forming method (Fig. 11) characterized by:

- a mask forming process for forming a mask having pattern-forming openings on a workpiece surface (S140);

- a pattern material supplying process for supplying a liquid-pattern material to the pattern-forming openings while also drying the liquid-pattern material (S142 with "Simultaneous Drying");

- an annealing process for annealing dried solute of the liquid-pattern material (S145); and

- a process for removing the mask from the workpiece (S146).

Independent Claim 20

The present invention, as recited in independent claim 20, is further directed to a pattern forming method (Fig. 9) characterized by:

- a mask forming process for forming a mask having pattern-forming openings on a workpiece surface (S120);

- a pattern material supplying process for supplying a liquid-pattern material to the pattern-forming openings (S122);

- a drying process for evaporating solvent in the liquid-pattern material (S123);

- an annealing process for annealing dried solute in the liquid-pattern material (S124); and

- a mask removal process for removing the mask from the workpiece (S125).

Independent Claim 21

The present invention, as recited in independent claim 21, is further directed to a pattern forming method (Fig. 7 and/or Fig. 14) characterized by:

a mask forming process for forming a mask having pattern-forming openings on a workpiece surface (S100);

a pattern material supplying process for supplying a liquid-pattern material to the pattern-forming openings (S102);

an adherent-liquid removal process for removing liquid-pattern material that adhered to the mask surface when the liquid-pattern material was supplied to the pattern-forming openings (S103);

a drying process for drying by evaporating solvent in from liquid-pattern material in the pattern-forming openings (S104);

a mask removal process for removing the mask from the workpiece after sequentially performing plural times the pattern material supply process, adherent-liquid removal process, and drying process (S104 of Fig. 7 and S171-S173 of Fig. 14)); and

an annealing process for annealing the dried solute (S106).

[0004] Semiconductor devices are manufactured by repeatedly performing film formation and film patterning operations. Fig. 33 and Fig. 34 are process diagrams showing an example of a conventional patterning process.

[00199] Fig. 13 is a flow chart of a seventh pattern forming method according to the present invention. The pattern forming method of this embodiment is used when pattern forming openings are already disposed on the surface of the workpiece 20, such as in combination with conventional processes. The mask forming process is therefore omitted in this seventh pattern forming method.

[00205] Fig. 14 is a flow chart of an eighth pattern forming method according to the present invention. The pattern forming method of this embodiment is also applied when pattern forming recesses are also disposed to the workpiece 20. This eighth pattern forming method first hydrophobic processes the surface of the workpiece 20 (step S170). This workpiece 20 hydrophobic process is as described previously.

[00208] By thus supplying the liquid pattern material to the pattern forming recesses a small amount at a time, and repeating the pattern material supply and pattern material drying steps, the formation of voids when the pattern material dries can be prevented, and a detailed pattern with low internal stress can be formed. Moreover, because unnecessary liquid pattern material adhering to the workpiece surface is removed before drying the liquid pattern material 312, excess material adhering to the workpiece 20 surface can be removed more easily than when dried material is removed.

Independent Claim 22

The present invention, as recited in independent claim 22, is further directed to a pattern forming method (Fig. 11), comprising:

a mask forming process for forming a mask having pattern-forming openings on a workpiece surface (S140);

a pattern material supplying process for supplying a liquid-pattern material to the mask openings (S142);

a drying process for drying by evaporating solvent from the liquid-pattern material in the pattern-forming openings (S143);

a solid-material removal process for removing dried solids of the liquid-pattern material that adhered to the mask surface when the liquid-pattern material was supplied to the pattern-forming openings (S144);

a mask removal process (S146) for removing the mask from the workpiece after sequentially performing plural times the pattern material supply process, drying process, and solid-material removal process (S142-S144); and

an annealing process for annealing the dried solute (S145).

It is noted that in Fig. 11, mask removal S146 is shown after the annealing process S145, it should be noted that the sequence of these two steps is described as design a choice based on the materials used in the pattern supply process S142 and in the mask forming process S140. This is explained at least in paragraphs [00276] and [00277], as follows.

[00276] The pattern film is then annealed and the mask 656 removed. The annealing temperature of the pattern film 660 and the carbonization temperature of the resist are first compared. *If the carbonization temperature of the resist film forming the mask 656 is higher than the annealing temperature of the pattern film 660, the pattern annealing process follows the drying process.*

[00277] However, *if the carbonization temperature of the resist film is lower than the annealing temperature of the pattern film 660*, the resist film (mask 656) will carbonize during the annealing process and removing the mask 656 will be difficult. In this case, therefore, *the mask removal process is performed first and then the pattern annealing process is performed.* It should be noted that because the carbonization temperature of PMMA, a typical resist, is approximately 260°C, and the annealing temperature of an ITO film is 500°C or higher, the resist removal process is performed first and then the annealing process is performed.

GROUND OF REJECTION TO BE REVIEWED ON APPEAL

Claims 1-22, are rejected under 35 U.S.C. §102(b) as being anticipated by EP0630044 A2 (Okumura et al., hereinafter referred to Okumura).

ARGUMENT

In paragraph 2 of the Final Office Action, the Examiner sets forth her rejection of Claims 1-22 under 35 U.S.C. §102(b) as being anticipated by Okumura. Specifically, it is asserted that all features of the present invention, are shown in Okumura's: abstract; col. 2, lines 24-57; col. 3, lines 14-58; col. 4, lines 1-56. Responses to some previously submitted applicant's arguments are listed in paragraph 3. In reference to paragraph 2, it is stated,

"immersing the substrate with openings to a predetermined solution to fill the opening with the material (solidified liquid pattern material, drying the liquid solution adhered onto the opening so as to form a layer in the opening, the SOG layer or SiO₂ layer is solidified, palladium layer (electrically conductive layer) formed in the openings)"

Applicants contend that Okumura does not show solidifying a solution, and particularly does not show solidifying a solution by means of a first heat-dry step (to produce solute by evaporation) followed by an annealing step. To better illustrate this, it may be helpful to discuss the relevant text of each of the cited Okumura citations noted above.

In regards to Okumura's abstract, the relevant text appears to be the seventh and tenth paragraphs of the abstract, which state,

Okumura Abstract, paragraphs 7 and 10.

"... immersing the substrate having the first patterned layer into a predetermined solution *to form a fourth layer* (45) selectively over the portions of the second layer uncovered by the first pattern layer; and

... characterized in that the first layer (41) is an insulating layer, the second layer (42) is a metal layer, third layer (43) is a photoresist layer, and *the fourth layer is a SiO₂ layer*, whereby the remainder of the second layer (42) constitutes a metal interconnect layer for the second semiconductor device.

As is stated in paragraph 7, the fourth layer (45) is formed by immersing the substrate into a predetermined solution, and as it is explained in paragraph 10, the fourth layer is a SiO₂ layer, which is an insulator. Thus it is self-apparent that the "predetermined solution" is not, and does not, precipitate a conductive

material, in direct contradiction to at least claims 1 and 7. As it will be further explained below, the SiO₂ is not formed by solidifying the "predetermined solution". Rather, SiO₂ is grown using a liquid phase deposition, i.e. LPD, method, which is typically favored due to it not requiring expensive equipment and it being suitable for use at ambient temperatures. The point is that the solution is not solidified, and remains in a solution form even after formation of the SiO₂ layer. Rather, the solution is subject to a chemically reaction that grows a layer of SiO₂ on exposed surfaces of the second layer (i.e. metal layer 42). The abstract does not teach nor suggest that the solution is solidified, and especially does not teach or suggest that the solution is solidified by application of a first heat-dry step to create dry solute by evaporation, followed by a heat anneal step to finish solidifying the dried solute.

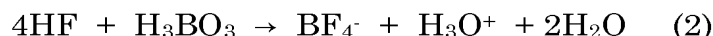
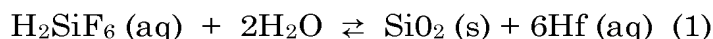
The next cited Okumura excerpt, col. 2, lines 24-57, describes Okumura's invention of using a layer of SiO₂ (grown by liquid phase deposition) as a mask to etch a metal layer (31, see Okumura Figs. 3A-3D) into separate conductive traces (31a, 31b, and 31c, see Fig. 3D). In the present case, the relevant text is the 10th paragraph in col. 2 (i.e. col. 2, lines 37-50), reproduced herein for convenience.

Okumura, col. 2, lines 37-50

" Next, the substrate 30 is immersed into a silicofluoride aqueous solution. In this step, a silicon oxide (SiO₂) layer 35 of about 1000 Å. is selectively formed at the area where the tungsten silicide (WSi) layer 31 is exposed, since the H₂SiF₆ and H₂O react to precipitate SiO₂. To selectively form the SiO₂ layer, the surface of the photoresist layer 33a and 33b are subjected to, e.g., an oxygen plasma, to change the surface thereof from a hydrophilic condition (having, e.g., -OH radical as an end radical) to a hydrophobic condition (having, e.g., -O radical as an end radical), preferably. (FIG. 3B) This process is referred to as a hydrophobic treatment hereafter."

As is clear from the above, the aqueous solution contains H₂SiF₆ and H₂O and chemically reacts to grow, i.e. precipitate, on exposed tungsten silicide (Wsi) layer 31 a layer of SiO₂. This process of growing silicon dioxide, i.e. SiO₂, is known as liquid phase deposition, LPD, of silicon dioxide, as is explained in

article "Development of Liquid Phase Deposition of Zirconium Oxide and Comparison to Silicon Dioxide", by Sampo Niskanen, Helsingin Matemaattikalukio, Nov. 19, 2000 (Exhibit A). Page 3 of the Niskanen article explains that an H_2SiF_6 aqueous solution reacts with water (i.e. H_2O) to form SiO_2 and a hydrogen fluoride, HF , byproduct. The HF byproduct may be neutralized by reacting with boric acid, H_3BO_3 to create a stable complex ion BF_4^- . Niskanen describes this reaction, as follows:



There are several points to be made. Firstly, it is self-evident that Okumura's solution is not "solidified", as is required in the present invention. That is, Okumura's solution remains a solution after the chemical reaction is complete, albeit in a chemically altered form. Furthermore, it cannot be sustained that the solid that is grown by the chemical reaction, i.e. SiO_2 , is a solidified form of the aqueous solution (H_2SiF_6 and H_2O) since SiO_2 is chemically different from the aqueous solution. Secondly, since SiO_2 is an insulator, it is likewise self-apparent that the solution is not, and does not, precipitate a conductive material. Thirdly, Okumura does not teach or suggest that his aqueous solution is solidified by drying the solution to precipitate a dried solute, that is subsequently annealed into a high quality solid trace (i.e. conductor layer). Fourthly, this process does not teach or suggest repeated applications of the aqueous solution, particularly since the mask is removed following the growth of SiO_2 .

Fifthly, the present invention further teaches two additional steps to be executed *before* solidifying the applied liquid-pattern material. As is recited in claim 5, for example, the present invention requires an "adherent-liquid removal process for removing liquid pattern material that adhered to the mask surface when the liquid-pattern material was supplied to the openings" *before* solidifying the liquid-pattern material. In other words, prior to the solidifying process, any liquid-pattern material not within the openings of the mask is removed. This is clearly in contradiction to Okumura's teaching that the substrate remain immersed in this solution during the growth of SiO_2 in order for the chemical

reaction to take place. If Okumura's substrate were removed from his aqueous solution so as to remove any aqueous solution that adhered to his mask prior to formation of his solid (i.e. SiO₂), then no solid could form since no chemical reaction on the substrate can take place outside of the solution.

The second additional step, recited at least in claim 7, explains that following the solidifying of the liquid pattern material, the present invention further includes, "a solid-material removal process for removing solidified elements of the liquid-pattern material that adhered to the mask surface when the liquid-pattern material was supplied to the pattern-forming openings." Okumura does not teach any such solid-material removal process. Furthermore, Okumura teaches that no solid SiO₂ is formed on his mask surface during his chemical LPD process. Specifically as is noted above in col. 2, lines 37-50, Okumura explains that his mask (i.e. photoresist layer 33a and 33b) is made hydrophobic to repel the aqueous solution, and that the SiO₂ grows only on exposed areas of his tungsten silicide (WSi) layer 31. Thus, it is self apparent that Okumura teaches that no solid grows on his mask, and thus no solid-material removal process is taught or suggested by Okumura's process.

Okumura col. 3, lines 14-58

The present Office Action further assert that the present invention is taught in Okumura col. 3, lines 14-58. In the present case, the relevant text is col. 3, lines 16-43, which state:

" FIGS. 4A to 4D are cross sectional views for explaining a second embodiment of the present invention. On a semiconductor substrate 40, a thermal oxide layer 41 is formed. On the oxide layer 41, an aluminium layer (A1) 42 of about 8000 Å. to be etched is formed by, e.g., sputtering. Then, a patterned photoresist pattern 43 of about 12,000 Å is formed on the A1 layer 42 using a conventional exposure and development technique. Next, a glass layer 44 is formed by a Spin on Glass (SOG) method following a baking treatment. (FIG. 4A) Then, a conventional etching process is carried out to remove the relatively thin glass layer formed on the photoresist 43, and to leave a portion of the relatively thick glass layer 44 formed where the photoresist layer 43 is not formed. Next, a hydrophobic treatment is carried out.

Then, the substrate is immersed into a silicofluoride aqueous solution to form a SiO₂ pattern 45 of about 2000 Å on the glass layer 44, selectively. (FIG. 4B)

Next, the photoresist pattern 43 is removed by, e.g., a wet etching. (FIG. 4C)

Then, an anisotropic etching, e.g., a RIE, is carried out to form a desired A1 wiring layer 42a and 42b using the SiO₂ pattern 45 as a mask. (FIG. 4D) Then, an etching for removing the SiO₂ layer 45 and the glass layer 44 is carried out (not shown)."

The Office Action asserts that this excerpt teaches a spin-on-glass, SOG, process where the glass is solidified by applying heat, i.e. in view of the baking treatment. Applicants had pointed out in a previous Office Action Response that in an SOG process, a drop of molten glass is typically placed in the middle of a silicon wafer (or other substrate), while the wafer is being spun so as to allow centrifugal force to evenly distribute the molten glass over the wafer and form a glass layer. As it is further known in the art, molten glass is solidified by *cooling*, not by *heating*. Indeed Okumura makes sure to note that his SOG process step *follows* a baking treatment, so as to assure that no high temperatures are applied to the solidified glass, otherwise the solidified glass would melt.

In a telephone interview with Examiner Chako-Davis, Applicants pointed out to the Examiner that the present invention teaches applying a heat treatment to the supplied liquid pattern material, and further teach that the liquid pattern material is solidified by the application of heat. That is, the present invention teaches solidifying the liquid pattern material by first applying heat to produce a dried solute by evaporation, and then applying heat to anneal the dried solute. Examiner Chako-Davis, however, contended that unless otherwise specified in the claims, the order of claim process steps may be rearranged to recreate the prior art, and thus she could place the claimed heat dry step prior to the step of supplying the liquid-pattern material. Applicants vehemently disagree since the order of the process steps is not only suggested by the order in which they are recited, but is strictly encoded into the text of the process steps by virtue of each current process step referencing a previous process step. For example, the presently claimed process steps cannot be

rearranged so as to apply the claim heat-dry step for drying the supplied liquid pattern material prior to applying the claim process step for supplying of the liquid pattern material in the first place: otherwise there would not be any liquid pattern material to be dried by the claim heat-dry step. Thus, Applicants reassert the position that it is inappropriate to rearrange the sequence of claim process steps in such a manner so as to contradict claim language, or to make nonsensical, the claimed invention.

Thus, it is clear that the molten glass in Okumura's SOG process does not read on the liquid pattern material of the present invention: firstly because it is not solidified by heat drying and/or heat annealing; secondly because it is an insulator, and not a conductor (as required by at least claims 1 and 7); thirdly because no dried solute is precipitated from the glass by evaporation; and fourthly because Okumura does not teach or suggest an SOG process where glass is distributed within a mask, and the glass is annealed after the mask is removed (this would re-melt the glass).

As it is further noted in the above excerpt, the SOG process is a preliminary process step in preparation for the growth of SiO₂. After the glass has been formed in the mask openings, Okumura explains that the mask is subjected to a hydrophobic treatment, and the substrate is then "immersed into a silicofluoride aqueous solution to form to form a SiO₂" in areas not covered by the mask. As is explained above, this process of growing SiO₂ is known as liquid phase deposition, and does not read on the present invention because: (1) the aqueous solution is not solidified; (2) the aqueous solution is not solidified by heat evaporation and heat annealing; (3) the precipitated solid SiO₂ is chemically distinct from the aqueous solution and is therefore not a solidified form of the aqueous solution; (4) and the precipitated solid is an insulator, not a conductor.

Okumura col. 4, lines 1-56

It is noted that Col. 4, lines 1-56 encompasses two complete process examples. The first, found in col. 4, lines 7-32, is substantially similar to the example of col. 3, lines 14-58 discussed immediately above. As is explained

above, neither the application of a baking treatment followed by a spin-on-glass step (col. 4, lines 13-14), nor the application of a SiO₂ growth step by liquid phase deposition (col. 4, lines 18-21) teach or suggest the present invention.

The second process example is found in col. 4, line 33 to col. 5, line 19 in reference to Figs. 6A-6D. In the present case, the relevant text is col. 4, lines 33-50 and col. 5, lines 17-19, reproduced herein for convenience.

" FIGS. 6A to 6D are drawings for explaining a fourth embodiment for forming a contact hole in a semiconductor device. On a semiconductor substrate 60, and insulating layer 61 is formed. Then, a polysilicon layer 62 of about 300 Å is formed on the insulating layer by, e.g., a low pressure CVD method. Next, a patterned photoresist layer 63 is formed on the polysilicon layer 62 using a conventional exposure and development technique. (FIG. 6A) *Then, a hydrophobic treatment of the photoresist layer 63 is carried out.*

Next, the substrate is immersed into a solution of palladium chloride (PdCl₂) to form a palladium layer 64 of less than 100 Å using an electroless plating method. Next, the substrate is immersed into a mixed solution of nickel sulfate (NiSO₄) and hypophosphite to form a nickel layer 65 of about 1000 Å. (FIG. 6B) ...

... The palladium layer 64 provides a good adhesion between the polysilicon layer 62 and the nickel 65."

In this example, Okumura shows forming a via using nickel electroless plating. Specifically, Okumura shows a two step electroless plating process wherein a first electroless plating process for forming a thin palladium layer 64 is followed by a second electroless plating process for forming a nickel layer 64 on the palladium layer 64. As Okumura explains immediately above, the "palladium layer 64 provides a good adhesion between the polysilicon layer 62 and the nickel 65." In other words, nickel may not plate well onto polysilicon, and an intermediate material, or activation layer, that adheres well to (i.e. react well with, or is catalytic to) both polysilicon and to nickel is placed between the polysilicon and the nickel. In Okumura's example, this activation material is palladium.

A similar process for forming a via using nickel electroless plating is described in article "Selective Electroless Metal Deposition for Integrated Circuit Fabrication", by Chiu H. Ting and M. Paunovic, *Journal of the Electrochemical*

Society, Vol. 136, No. 2, February 1989, pages 146-462, (Exhibit B), (hereinafter Ting). In discussing electroless plating in their "Deposition Process" section on page 456, Ting explains that a benefit of electroless plating is that, "the deposition process is highly favorable at chemically active surfaces such as silicon and aluminum against the chemically inert dielectric surfaces such as silicon dioxide or photoresist". Since chemically inert materials, such as a photoresist mask do not chemically react and do not experience any plating, it is noted that no solids adhere to the photoresist mask in an electroless plating process. Ting further explains that electroless plating is a chemical reaction in which a chemically active surface reacts with a solution to exchanging atoms with the solution. In this manner, the chemically active surface acquires a layer of atoms from the solution, and the solution incorporates atoms from the chemically active surface. As the surface is covered by the layer of atoms, however, the chemical reaction slows and finally stops, such that electroless plating is a self-limiting reaction. Ting explains that the reaction may be enhanced by applying a "reducing agent", such as hypophosphite. Ting provides an example toward the bottom of the first column on page 457 wherein a solution of nickel and hypophosphite is used to form a nickel layer. The last paragraph on the right-column of page 457 further explains that some surfaces are not catalytic to nickel deposition, in which case the surface maybe activated using a layer of palladium, in a manner similar to Okumura's example.

In a previous Office Action response, Applicants had pointed out that electroless plating is not equivalent to solidifying a liquid-pattern material, and is particularly not equivalent to solidifying a liquid by a first heat-drying step to produce dried solute followed by an annealing step. This is particularly true since an electroless plating process produces byproducts that are released into the solution such that the solution is not solidified at the end of electroless plating process. That is, the solution remains a solution, but in a chemically altered form. Furthermore, the plated layer (i.e. pure palladium or nickel) is chemically different from the solutions from which they are extracted (i.e. palladium chloride (PbC12) or nickel sulfate (NiSo4), respectively). Since a

plated solid is different from the solution from which it is extracted, the plated solid cannot be said to represent a solid form of the solution.

In the aforementioned telephone interview with Chako-Davis, it was pointed out that Okura's palladium layer 64 is constructed by electroless plating in a palladium chloride solution. Examiner Chako-Davis appeared to agree that electroless plating is not equivalent to solidifying a liquid-pattern material (particularly solidifying by producing dried solute through evaporation). However, in the present Final Rejection, the Office Action sites the formation of nickel layer 65 from a solution of nickel sulfate as being equivalent to the presently claimed solidified liquid pattern material. It would appear that the Office Action is not convinced that the nickel layer is the result of an electroless plating process, in the same manner as the palladium layer is the result of electroless plating. However, as is explained above in reference to the Ting article, Okumura's process recitation is consistent with a via forming process requiring two separate electroless plating processes. This is highlighted by Okumura, himself, in col. 7, lines 43-47, wherein Okumura explains that nickel layer 65 in the example of Fig. 6 is formed by electroless plating (i.e. a non-electric plating process). Specifically, Okumura state,

" In the examples of Figures 3, 4, 5 and 7, a SiO₂ layer formed by a precipitation is used as a mask layer. However, it is possible to use a nickel layer formed by an non-electrical plating process, as used in Fig. 6, as a mask layer, and vice versa. Thus, in each embodiment, either a SiO₂ layer or a nickel layer may be used as the mask layer."

Thus, applicants assert that Okura's nickel electroless plating process does not read upon the present invention's requirement of solidifying a liquid.

It is noted that the Office Action cites Okumura's two plating process (i.e. a first electroless plating process to form a palladium layer followed by a second electroless plating process for form a nickel layer) to read on the present invention's recitation of repeating the steps of providing the liquid pattern material followed by step of solidifying the provided liquid pattern material, prior to a final annealing process step or a mask removal step. Applicants respectfully point out that the claim language require that specific process steps

be repeated, and thus the liquid pattern material would be understood to be the same each time the specific steps are repeated. This is contrary to Okumura's teaching wherein the first solution is palladium chloride to plate a layer of palladium, and the second solution is nickel sulfate to plate a layer of nickel. Nonetheless, as is explained above, electroless plating does not read on the presently claimed liquid-pattern material, nor on the process step of solidifying the liquid-pattern material, nor solidifying the liquid-pattern material by a heat drying process to produce solute by evaporation followed by a step to heat annealing the solute. It is further noted that Okumura does not teach or suggest any annealing step following the formation of a nickel plate layer.

In paragraph 3 of the Final Office Action, responses A to D to previously submitted arguments are provided. It is believed that applicant's position has been clarified above. In regards to item (D), however, it is noted that the Office Action asserts that,

"Okumura, in col. 3, lines 16-32, discloses that spin-on-glass material is formed (spray or spin coating the spin-on-glass liquid material) in the openings of the photoresist mask, followed by baking. Baking involves evaporating as well as annealing since baking involves heating to high temperatures."

Applicants respectfully point that in "col. 3, lines 16-32" Okumura does not disclose that a spin-on-glass process is followed by baking. As is explained above, this would result in re-melting the glass layer and thus render Okumura's process inoperable. Rather Okumura states in col. 3, lines 23-25 that, "...glass layer 44 is formed by a Spin on Glass (SOG) method following a baking treatment." As is clear from this quote, Okumura explains that his SOG process follows his baking treatment.

Further in response to the assertion that baking encompasses both drying and annealing, since it has been shown that Okumura's baking step precedes his SOG step, combining of the drying and annealing steps into Okumura's baking step still does not achieve the present invention. Nonetheless, Applicants feel compelled to explain that while it is true that if baking is conducted at a sufficiently high temperature, one may achieve both drying and annealing, but

such is not always practical, or optimal, and may result in an inferior product. This is explained at least in paragraph 00173 of the specification of the present invention, wherein it state,

[Para. 00173] ... Moreover, because the liquid pattern material 312 is annealed in the pattern annealing process *after* drying in the pattern drying process in this first pattern forming method, the formation of internal voids and the *formation of deformation recesses in the formed pattern surface when the liquid pattern material 312 solidifies can be prevented.*

Thus, applicants contend that it improper to combined separately recited process steps when such a combination would result in a substantially different product. Furthermore, applicants point out that at least claims 2, 3, 5, 6, 8, 9, 16, and 21 require that additional intervening process steps be executed between the heat drying step and the annealing step. It is clear that in such cases, the drying step and annealing steps cannot be combined without omitting the intervening process steps.

Having discussed the cited prior art, and the Office Action's position, separate arguments for the claims is provided below, with reference to the above discussion.

Claims 1, 10, 11, 12, 13, 14

Claim 1 requires, inter alia, "supplying and solidifying *an electrically conductive liquid pattern material* in the pattern-forming openings of the mask". As is explained above, Okumura's liquid phase deposition (LPD) of SiO₂ and electroless plating processes do not solidify a liquid (i.e. their respective solutions remain in solution form after their production of a solid), nor is the solid that results from their respective chemical reactions a representative form of the solution from which they are extracted. That is, SiO₂ is not a solid form of the solution from which it is extracted, silicofluoride aqueous solution (i.e. H₂SiF₆(aq) + H₂O); palladium is not a solid form of the solution from which it is extracted, palladium chloride (PbCl₂); and nickel is not a solid form of the solution form which it is extracted, nickel sulfate (NiSO₄) and hypophosphite. This difference is particularly self-evident when one considers that palladium chloride and

nickel sulfate are both salts, while palladium and nickel are metals. Thus, none of the solids can be asserted to represent solid forms of (or solidified samples of) the solution from which they were extracted.

In regards to Okumura' use of spin on glass, SOG, since glass is an electrical insulator, it is clear that glass does not read on the claimed "*electrically conductive* liquid pattern material", as would be required by the present the rejections under 35 U.S.C. §102(b). Furthermore, since an electrical insulator is directly contrary to an electrical conductor, it is not obvious to replace one for the other.

Dependent claim 12 further clarifies that, "the liquid-pattern material is solidified by applying heat." As is explained above, none of Okumura's process steps teach solidifying an electrically conductive liquid by applying heat.

Dependent claim 13 further clarifies that the electrically conductive liquid pattern material is solidified by applying a first drying step to produce dried solute by evaporation (as it is known in the art, once a solvent has been extracted from a liquid, i.e. solution, the resultant dried solvent particles are termed a solute since they are no longer dissolved in the liquid). This drying step is followed by an annealing step to anneal the dried solute. Since the annealing step anneals solute produce in the drying step, it is clear that the annealing step must follow the drying step. As is further explained above, Okumura is silent on any process for solidifying a liquid (particularly an electrically conductive liquid) by producing dried solute by evaporation, followed by annealing the dried solute.

Claim 15 further explains that, "the liquid-pattern material is solidified after removing liquid-pattern material that adhered to the mask surface when the liquid-pattern material was supplied to the pattern-forming openings". As is explained above, the only process that remotely relates to the this claim is Okumura' electroless process since it produces a conductive layer. However, as is explained above, the electroless plating process requires that the substrate be immersed in a chemical solution. If the substrate is removed from the solution, then no plating can occur. Therefore, it makes no sense to assert that Okumura teaches that the liquid pattern material is solidified (or that a solid is extracted

from a liquid) after the substrate is removed from the solution, as would be required in order to remove liquid-pattern material that adheres to the mask surface. Furthermore, Okumura explains that no material adheres to his mask due it having been made hydrophobic to repel liquid. Additionally, since the mask is chemically inert, it does not react with the solution.

Claim 2, 18

Claim 2 requires that the liquid pattern material be dried while it is being supplied to the pattern-forming opening of the mask. None of Okumura's cited processes teach or suggest such a step. Both of Okumura's processes for LPD of SiO₂ and electroless plating required that the substrate remain immersed in a solution. In the case of SOG, the glass is solidified by cooling, not drying (especially not heat drying).

The language of claim 2 does not restrict the application of the annealing step to being after the mask removal step. Therefore, claim 18 teaches that the mask removal step and the annealing step may be executed simultaneously. Okumura does not teach or suggest a combined mask removal and annealing step.

Claim 3

Claim 3 clearly recites that after the liquid-pattern material is supplied, it is subjected to "a drying process for evaporating solvent in the liquid-pattern material". As it would be understood, this evaporation process by drying produces the dried solute that constituted the solvent in the liquid-pattern material. After the dried solute has been produced, claim 3 requires removal of the mask, followed by "annealing process for annealing dried solute in the liquid-pattern material." These processes steps clearly explain a solid in the present invention is produced by extracting dried solute from the liquid-pattern material by evaporation, and then annealing the dried solute. Clearly, none of Okumura's cite processes (i.e. LPD, SOG, or electroless plating) described this method of solidifying a liquid. Furthermore, none of Okumura's cited processes teach or suggest an annealing step after the mask has been removed.

Claim 4

Claim 4 describes, "supplying an *electrically conductive* liquid-pattern material to the pattern-forming openings." Thus, neither of Okumura's processes for LPD deposition of SiO₂, or SOG read on claim 4 since both SiO₂ and glass are both insulators and not electrically conductive.

Furthermore, as is explained above, Okumura's electroless plating process does not read on the claimed step of solidifying the liquid-pattern material primarily because Okumura's extracted solid is dissimilar to the solution form which it is extracted, and secondly because Okumura's solution is not solidified during the formation of a solid plating material.

Since Okumura does not teach or suggest either of the above two step, it is clear that he does not teach nor suggest their repeated application prior to removal of the mask.

Claim 5

Claim 5 recites "an adherent-liquid removal process for removing liquid pattern material that adhered to the mask surface when the liquid-pattern material was supplied to the openings." As is explained above, both LPD of SiO₂ and electroless plating require that the substrate remain immersed in a solution during the forming of a solid on the substrate. Since the mask is attached to the substrate, liquid cannot be removed from the mask without also removing the substrate from the solution, which would prevent the forming of a solid on the substrate. As it is further explained above, not only does Okumura teach that his hydrophobic treatment prevents liquid from adhering to his mask, the mask is chemically inert to the electroless plating process. Thus Okumura teaches that no liquid adheres to his mask, and thus teach away from the claimed adherent-liquid removal process.

As is further explained above, Okumura does not teach a solidifying processes consisting of a first drying process to produce dried solute by evaporation, followed by an annealing step for annealing the produced dried solute. It must be emphasized that the claim language states, "annealing the dried solute after sequentially performing plural times the pattern material

supply process, adherent-liquid removal process, and drying process", such that it is not possible to combine the annealing step into the drying step, as is suggested by the Office Action. This is the case not only because of the intervening steps between the drying step and the annealing step, but also because the annealing step references the dried solute created by the drying step. Thus, the drying step should be implemented prior to the annealing step in order to produce the dried solute required in the annealing step.

Claims 6, 16, 17

Claim 6 recites a drying process for evaporating solvents from the liquid-pattern material. As it is known, the solvent once dried from a liquid is termed a solute. Thus, claim 6 further recites, "an annealing process for annealing the dried solute after sequentially performing plural times the pattern material supply process and drying process."

As is explained above, Okumura is silent on any process of producing a solid from a liquid by first producing dried solute by evaporation, followed by annealing the dried solute.

Claim 16 further requires that the annealing process be performed after removing the mask. Okumura is silent on any process that teaches an annealing step *after* a mask removal step.

Claim 7

Claim 7 recites supplying an electrically conductive liquid-pattern material. As is explained above, this requirement prevents application of Okumura's LPD of SiO₂ and SOG since both SiO₂ and glass are electrical insulators.

As is also explained above, the process of producing solid metal by electroless plating does not read on the claimed process of "solidifying the liquid-pattern material", since electroless plating does not solidify its solution nor is the plated metal a solid form of the solution.

Claim 7 further recites, "a solid-material removal process for removing solidified elements of the liquid-pattern material that adhered to the mask surface when the liquid-pattern material was supplied to the pattern-forming openings." As is explained above, the mask material is chemically inert, and thus no solids form on it.

In the present invention, however, since the solid is formed by producing dried solute by evaporation, it may occur that solid, solute particles may adhere to the mask which where previously repelled from the mask when the particles were a solvent in liquid due to the mask having been made hydrophobic.

Lastly, it is clear that Okumura does not teach or suggest repeated applications of "the pattern material supply process, solidifying process, *and solid-material removal process*" prior to removing the mask.

Claim 8

Like claim 7, claim 8 recites a drying process to produce solute by evaporation, and recites a solid-material removal process for removing solids that adhered to the mask surface. As is explained in reference to claim 7, above, Okumura does not teach or suggest these process step.

Claim 8 further recites an annealing step for annealing the dried solute, "after sequentially performing plural times the pattern material supply process, drying process, solid-material removal process." As is also explained above, Okumura does is silent on any step for annealing dried solute produced from a liquid by evaporation using a drying process.

Claim 9

Like claim 8, claim 9 recites producing dried solute from a liquid-pattern material through evaporation by mean of drying process, and recites a solid-material removal processes followed by a step for annealing the dried solute. Claim 9, however, further requires that the mask not be removed until, "sequentially performing plural times the pattern material supply process,

drying process, solid-material removal process, and annealing process". Since Okumura does not teach or suggest these individual steps, neither does he teach or suggest their repeated application prior to removal of the mask.

Claim 19

Claim 19 teaches a combined step of supplying a liquid-pattern material while also drying the liquid-pattern material. As is explained above in reference to claim 2, this is not taught or suggested by Okumura.

Claim 19 further recites that the liquid-pattern material is solidified by a heat dry step to produce dried solute by evaporation, and an annealing step for annealing the dried solute. Again, Okumura is silent on any process for producing dried solute by evaporation, and annealing the produced dried solute.

Claim 20

Claim 20 recites a root aspect of the present invention, i.e. that of solidifying liquid pattern material by means of a drying process for evaporating solvent in the liquid-pattern material, followed by an annealing process for annealing dried solute produced by the drying process. As is explained above, Okumura is silent on any process of solidifying a liquid pattern material by producing dried solute by evaporation, followed by annealing the dried solute.

Claim 21

Claim 21 recites "an adherent-liquid removal process" *prior* to the solidifying steps. As is explained above, this is contrary to Okumura's LPD of SiO₂ and electroless process since these processes require that the substrate remain immersed in a solution in order to form a solid on the substrate. Furthermore in regards to SOG, it is self-apparent that the molten glass cannot be removed from the mask prior to solidifying the glass. As it is known in the art, and as is recited by Okumura, after the SOG process, the solid glass is

removed from the mask by etching. Okumura does not teach or suggest any step for removing liquid glass from the mask prior to solidifying the glass.

Not only does claim 21 recite the specific method of solidifying the liquid-pattern material as consisting of a drying step for producing dried solute by evaporation and a separate annealing step for annealing the dried solute produced in the drying step, claim 21 further prevents the annealing step from being combined with the drying step by requiring an intervening step of removing the mask after repeating "the pattern material supply process, adherent-liquid removal process, and drying process."

As is explained above, Okumura is silent on any liquid solidifying process consisting of a drying step for forming dried solute by evaporation followed by an annealing step.

Claim 22

Claim 22 again recites the present method of solidifying a solvent by a first drying step to produce dried solute by evaporation followed by an annealing step for annealing the dried solute. Claim 22, further recites a solid-material removal process for removing dried solids of the liquid-pattern material that adhere to the mask surface when the liquid-pattern material was supplied. As is explained above, Okumura teaches that no liquid adheres to his mask, and therefore no solid adhere to his mask. That is, Okumura teaches that no solid adheres to his mask during his LPD of SiO₂ and electroless plating process.

Although a solid (i.e. glass) is removed from the mask by etching following the SOG process, the SOG process does not read on the present solidifying method. That is, an SOG process does not solidify glass by through an evaporation step to produce dried solute and an anneal step to anneal the dried solute.

Lastly, Claim 22 teaches that the anneal step is separated from the drying step by a mask removal process that is executed only after repeated application

of "the pattern material supply process, drying process, and solid-material removal process."

CONCLUSION

It is respectfully submitted that the Examiner seeks to recreate the present invention in the Okumura reference by impermissible rearrangement of claim process steps, reading far more into the prior art than is reasonable, interchanging steps from a prior art insulator forming method (SOG or LPD) into a prior art conductor forming (electroless plating), overlooking key claim language (such as the meaning of solidifying a liquid), and neglecting claim processes steps (such as solidifying a liquid specifically by heat-drying the liquid to produce dried solute by evaporation and then annealing the produced dried solute). The Examiner has failed to meet the burden under the law with regard to showing either anticipation or obviousness of applicants' invention as particularly claimed.

Applicants therefore request that the Board reverse the Examiner's final rejection of Claims 1-22.

Respectfully submitted,

/Rosalio Haro/
Rosalio Haro
Registration No. 42,633

Please address all correspondence to:

Epson Research and Development, Inc.
Intellectual Property Department
2580 Orchard Parkway, Suite 225
San Jose, CA 95131
Telephone: (408) 952-6131
Facsimile: (408) 954-9058
Customer No. 20178
Date: May 15, 2007
Customer No. 20178
Brief_on_Appeal.doc

CLAIMS APPENDIX

1. A pattern forming method characterized by forming a mask having pattern-forming openings on a workpiece surface, and then supplying and solidifying an electrically conductive liquid pattern material in the pattern-forming openings of the mask.

2. A pattern forming method comprising:

- a mask forming process for forming a mask having pattern-forming openings on a workpiece surface;

- a pattern material supplying process for supplying a liquid-pattern material to the pattern-forming openings while also drying the liquid-pattern material;

- a process for removing the mask from the workpiece; and

- an annealing process for annealing dried solute of the liquid-pattern material.

3. A pattern forming method comprising:

- a mask forming process for forming a mask having pattern-forming openings on a workpiece surface;

- a pattern material supplying process for supplying a liquid-pattern material to the pattern-forming openings;

- a drying process for evaporating solvent in the liquid-pattern material;

- a mask removal process for removing the mask from the workpiece; and

- an annealing process for annealing dried solute in the liquid-pattern material.

4. A pattern forming method comprising:

- a mask forming process for forming a mask having pattern-forming openings on a workpiece surface;

- a pattern material supplying process for supplying an electrically conductive liquid-pattern material to the pattern-forming openings;

- a solidifying process for solidifying the liquid-pattern material supplied into the pattern-forming openings; and

a mask removal process for removing the mask from the workpiece after sequentially performing plural times the pattern material supply process and solidifying process.

5. A pattern forming method comprising:

a mask forming process for forming a mask having pattern-forming openings on a workpiece surface;

a pattern material supplying process for supplying a liquid-pattern material to the pattern-forming openings;

an adherent-liquid removal process for removing liquid pattern material that adhered to the mask surface when the liquid-pattern material was supplied to the openings;

a drying process for drying by evaporating solvent from the liquid-pattern material in the pattern-forming openings;

an annealing process for annealing the dried solute after sequentially performing plural times the pattern material supply process, adherent-liquid removal process, and drying process; and

a mask removal process for removing the mask from the workpiece.

6. A pattern forming method comprising:

a mask forming process for forming a mask having pattern-forming openings on a workpiece surface;

a pattern material supplying process for supplying a liquid-pattern material to the pattern-forming openings;

a drying process for drying by evaporating solvents from the liquid-pattern material in the pattern-forming openings; and

an annealing process for annealing the dried solute after sequentially performing plural times the pattern material supply process and drying process.

7. A pattern forming method comprising:

a mask forming process for forming a mask having pattern-forming openings on a workpiece surface;

a pattern material supplying process for supplying an electrically conductive liquid-pattern material to the pattern-forming openings;

a solidifying process for solidifying the liquid-pattern material supplied into the pattern-forming openings;

a solid-material removal process for removing solidified elements of the liquid-pattern material that adhered to the mask surface when the liquid-pattern material was supplied to the pattern-forming openings; and

a mask removal process for removing the mask from the workpiece after sequentially performing plural times the pattern material supply process, solidifying process, and solid-material removal process.

8. A pattern forming method comprising:

a mask forming process for forming a mask having pattern-forming openings on a workpiece surface;

a pattern material supplying process for supplying a liquid-pattern material to the mask openings;

a drying process for drying by evaporating solvent from the liquid-pattern material in the pattern-forming openings;

a solid-material removal process for removing dried solids of the liquid-pattern material that adhered to the mask surface when the liquid-pattern material was supplied to the pattern-forming openings;

an annealing process for annealing the dried solute after sequentially performing plural times the pattern material supply process, drying process, solid-material removal process; and

a mask removal process for removing the mask from the workpiece.

9. A pattern forming method comprising:

a mask forming process for forming a mask having pattern-forming openings on a workpiece surface;

a pattern material supplying process for supplying a liquid-pattern material to the mask openings;

a drying process for drying by evaporating solvent from the liquid-pattern material in the pattern-forming openings;

a solid-material removal process for removing dried solids of the liquid-pattern material that adhered to the mask surface when the liquid-pattern material was supplied to the pattern-forming openings;

an annealing process for annealing the dried solute; and

a mask removal process for removing the mask from the workpiece after sequentially performing plural times the pattern material supply process, drying process, solid-material removal process, and annealing process.

10. A pattern forming method as described in claim 1, wherein the mask has hydrophobic properties on at least the surface thereof for repelling the liquid pattern material.

11. A pattern forming method as described in claim 1, wherein the mask is hydrophobic for repelling the liquid pattern material.

12. A pattern forming method as described in claim 1, wherein the liquid-pattern material is solidified by applying heat.

13. A pattern forming method as described in claim 12, wherein heating and solidifying the liquid-pattern material comprises a drying process for evaporating solvent in the liquid pattern material, and an annealing process for annealing the dried solute.

14. A pattern forming method as described in claim 1, wherein the mask is removed from the workpiece after solidifying the liquid pattern material.

15. A pattern forming method as described in claim 1, wherein:

the liquid-pattern material is solidified after removing liquid-pattern material that adhered to the mask surface when the liquid-pattern material was supplied to the pattern-forming openings.

16. A pattern forming method as described in claim 6, wherein the annealing process is performed after removing the mask from the workpiece.

17. A pattern forming method as described in claim 6, wherein the mask is removed from the workpiece after the annealing process.

18. A pattern forming method as described in claim 2, wherein the process for removing the mask and the annealing process are performed simultaneously.

19. A pattern forming method comprising:

- a mask forming process for forming a mask having pattern-forming openings on a workpiece surface;

- a pattern material supplying process for supplying a liquid-pattern material to the pattern-forming openings while also drying the liquid-pattern material;

- an annealing process for annealing dried solute of the liquid-pattern material; and

- a process for removing the mask from the workpiece.

20. A pattern forming method comprising:

- a mask forming process for forming a mask having pattern-forming openings on a workpiece surface;

- a pattern material supplying process for supplying a liquid-pattern material to the pattern-forming openings;

- a drying process for evaporating solvent in the liquid-pattern material;

- an annealing process for annealing dried solute in the liquid-pattern material; and

- a mask removal process for removing the mask from the workpiece.

21. A pattern forming method comprising:

- a mask forming process for forming a mask having pattern-forming openings on a workpiece surface;

- a pattern material supplying process for supplying a liquid-pattern material to the pattern-forming openings;

- an adherent-liquid removal process for removing liquid-pattern material that adhered to the mask surface when the liquid-pattern material was supplied to the pattern-forming openings;

- a drying process for drying by evaporating solvent in from liquid-pattern material in the pattern-forming openings;

a mask removal process for removing the mask from the workpiece after sequentially performing plural times the pattern material supply process, adherent-liquid removal process, and drying process; and

an annealing process for annealing the dried solute.

22. A pattern forming method comprising:

a mask forming process for forming a mask having pattern-forming openings on a workpiece surface;

a pattern material supplying process for supplying a liquid-pattern material to the mask openings;

a drying process for drying by evaporating solvent from the liquid-pattern material in the pattern-forming openings;

a solid-material removal process for removing dried solids of the liquid-pattern material that adhered to the mask surface when the liquid-pattern material was supplied to the pattern-forming openings;

a mask removal process for removing the mask from the workpiece after sequentially performing plural times the pattern material supply process, drying process, and solid-material removal process; and

an annealing process for annealing the dried solute.

EVIDENCE APPENDIXExhibit A

"Development of Liquid Phase Deposition of Zirconium Oxide and Comparison to Silicon Dioxide", by Sampo Niskanen, Helsingin Matemaattikalukio, Nov. 19, 2000, <http://users.tkk.fi/~spniskan/LPD/lpd.html>

Exhibit B

"Selective Electroless Metal Deposition for Integrated Circuit Fabrication", by Chiu H. Ting and M. Paunovic, Journal of the Electrochemical Society, Vol. 136, No. 2, February 1989, pages 146-462,

RELATED PROCEEDINGS APPENDIX

N/A

Development of Liquid Phase Deposition of Zirconium Oxide and Comparison to Silicon Dioxide

Sampo Niskanen
Helsingin matematiikkalukio

19th November 2000

Abstract:

In a recently-developed liquid phase deposition (LPD) process silicon dioxide thin films are deposited from a solution of hexafluorosilicic acid (H_2SiF_6) supersaturated with SiO_2 by boric acid (H_3BO_3) addition. In this study, an analogous process for zirconium oxide is attempted and compared to the process with SiO_2 . The effects of boric acid, H_2ZrF_6 and ammonia concentrations are studied along with differing solution preparation routes. Films of 10-70 nm thickness are achieved, though the determination of their exact composition requires further study.

Contents

- 1 Introduction
 - 1.1 Silicon dioxide thin films
 - 1.2 Liquid phase deposition
 - 1.3 Other oxides
- 2 Experimental methods
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 - 3.1 Films grown
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- 4 Discussion
 - 4.1 Closer inspection of the LPD process
 - 4.2 Precipitation analysis
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- 5 Conclusion

AcknowledgementsAppendices**A** Test results of ellipsometer accuracy**B** Molarity and percentage correspondenceBibliography

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 - 3 Solubility of silicon and zirconium compounds
 - 4 Experimental parameters and results of LPD-SiO₂ with NH₃ addition
 - 5 Longer LPD-SiO₂ results for test of ellipsometer's accuracy
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1 Introduction

1.1 Silicon dioxide thin films

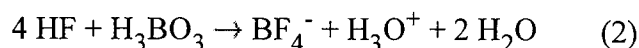
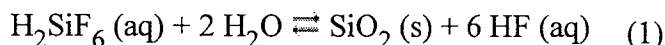
Silicon dioxide thin films are used in many industrial areas. SiO₂ films are used in some anti-reflection coatings and as an ion barrier in flat panel displays such as liquid crystal displays (LCD) and electroluminescent displays (ELD). It is also the most important insulating material in the fabrication of semiconductor devices. It is used for example as the gate insulator of metal-oxide-semiconductor (MOS) transistors and as masks in very large scale integration (VLSI) circuit processes.

There are many ways to form SiO₂ thin films, *e.g.* thermal oxidation (when the substrate is silicon), chemical vapor deposition (CVD), electron-beam evaporation and sputtering. All those methods require processing temperatures of several hundred degrees centigrade. Many also require expensive vacuum equipment and cannot be applied well to large surface areas.

1.2 Liquid phase deposition

Recently a new process called liquid phase deposition (LPD) has been developed, in which silicon dioxide is deposited while the substrate is immersed in a solution of hexafluorosilicic acid (H_2SiF_6) supersaturated with SiO_2 [1,2]. It does not require expensive equipment and the oxide can be deposited below 50°C and applied to a large and uneven surface. The oxide is furthermore grown selectively on the substrate and no growth occurs on materials such as photoresist.

The process is achieved by supersaturating a solution of H_2SiF_6 with SiO_2 by boric acid addition according to the following reactions:



Boric acid reacts with hydrofluoric acid creating a stable complex ion BF_4^- . This reduces the concentration of hydrofluoric acid and causes equilibrium (1) to shift to the right according to Le Chatelier's principle. This can also be accomplished by adding aluminum to the growth solution, where it reacts with HF to produce AlF_3 [3]. This model of growth is, though, oversimplified and does not explain the selective growth. The selective growth is further discussed in section 4.1.

Figure 1 shows a schematic diagram of the process, including two routes as described by Chang *et al.* [2]. The difference in the routes is the order of saturating the H_2SiF_6 solution and diluting it with water. It has been noted that using route I (saturation before dilution) results in a notably higher growth rate [2,4]. Chang *et al.* proposed that this is due to the role of water as a reagent, not only as a solvent. This means that the addition of water shifts reaction (1) to the right. In route II, the added SiO_2 then functions as a substrate actually depleting the solution of SiO_2 instead of saturating it.

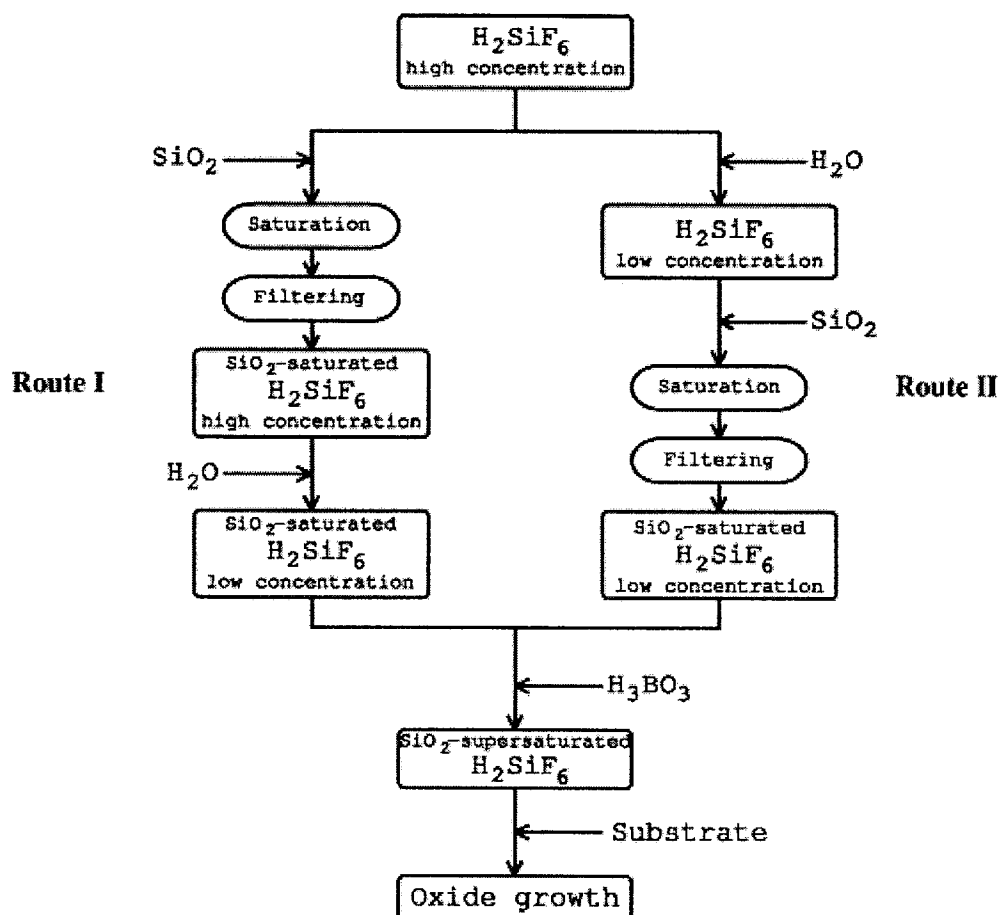


Figure 1: Schematic diagram of LPD- SiO_2

1.3 Other oxides

Liquid phase deposition is not limited to the formation of silicon dioxide layers. For example iron oxide [5] and vanadium oxide [6] can be deposited with a similar liquid phase process, whereas titanium oxide has been grown with an identical process using a H_2TiF_6 solution supersaturated with TiO_2 [7,8].

Another metal for which similar hexafluoro-complexes exist and are commercially available is zirconium. This suggests that a similar LPD process for ZrO_2 deposition might be possible, which would be an intriguing alternative to current deposition methods, such as atomic layer CVD (ALCVD) and sputtering. Zirconium oxide films are used in optical coatings on account of their high refractive index (2.05 at $\lambda = 500 \text{ nm}$) and high transparency over a large range of wavelengths (from near-UV at 300 nm to IR at 8 μm) [9].

In this research, I attempted to develop a method for zirconium oxide coating by directly substituting Si with Zr in the LPD process. Only one previous reference of LPD- ZrO_2 was found [10], a Japanese patent of which only the abstract was available in English. In the abstract ZrO_2 layers are claimed to have been deposited on soda-lime glass by adding aluminum chloride (AlCl_3) to hexafluorozirconic acid (H_2ZrF_6) and achieving thicknesses of 78 and 20 nm in 16 hours. This could not be tested due to the lack of necessary chemicals and time.

2 Experimental methods

Many experiments were made trying to grow ZrO_2 by means of LPD under varying conditions. The effects of different concentrations of H_2ZrF_6 and boric acid were studied along with different saturation levels, growth temperatures and preparation routes of H_2ZrF_6 . Also differing pH levels were tested by replacing boric acid by ammonium borate or ammonium. Source materials were 98 wt-% H_2ZrF_6 (7.6 mol/dm^3 , ABCR), boric acid powder (99.5 %, J. T. Baker) and 25 wt-% NH_3 (13.4 mol/dm^3 , Merck).

As the delivery of commercial ZrO_2 powder had been delayed, I decided to saturate the H_2ZrF_6 solution in several experiments with the precipitate formed in the reaction between H_2ZrF_6 and ammonia. I made the precipitate from waste H_2ZrF_6 (containing *ca.* 35 wt-% H_2ZrF_6 , 60 wt-% water, 3 wt-% ammonia and 2 wt-% boric acid) by adding about half of the volume 25 wt-% ammonia to it. The precipitate was then filtered, washed several times with water and dried in an oven at about 90°C for 15 hours and then at 120°C for 5 hours. It was then ground up to a powder with the largest pieces being about 2 mm in diameter. The precipitate was studied by thermogravimetry with a Seiko Instruments TG/DTA-320 thermobalance with an airflow of 80 ml/min.

Four different saturation types were tested: (i) no saturation of the 98 wt-% (7.6 mol/dm^3) H_2ZrF_6 (ii) saturating the 7.6 mol/dm^3 H_2ZrF_6 with the precipitate described above (route I) (iii) saturating 1.9 mol/dm^3 H_2ZrF_6 (1:3 ratio of H_2ZrF_6 and water) with the precipitate (route II) and (iv) saturating 1.9 mol/dm^3 H_2ZrF_6 with commercial ZrO_2 (99.7 %, Alfa Aesar) (route II). It was noted that several times more precipitate was required to saturate the diluted H_2ZrF_6 , than 98 wt-% H_2ZrF_6 .

The experiments were performed on a magnetic hotplate stirrer with external temperature probe. Unfortunately the probe broke at the very beginning and no replacement was available. It had to be wrapped in plastic for most of the experiments, reducing the accuracy of the measurement. The given temperatures are probably within a range of $\pm 2^\circ\text{C}$.

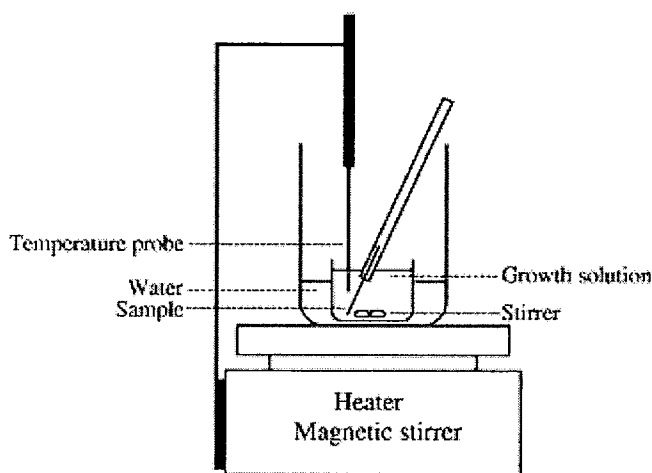


Figure 2: Experimental setup of deposition

The saturation was done on a magnetic stirrer overnight ($\sim 16 \text{ h}$, the exact saturation times may vary) at room temperature. The solution was then filtered through a $0.2 \mu\text{m}$ filter prior to deposition. The boric acid (or other HF scavenger) was then added and the solution was heated to 35°C , unless mentioned otherwise. The magnetic stirrer was at approximately 250 rpm. As the substrate pieces of a p-type (100) silicon wafer were used. Figure 2 shows the experimental setup for the deposition.

After deposition, the samples were rinsed in water and dried with nitrogen. The films were examined by means of ellipsometry with a Philips SD 2300 ellipsometer. The ellipsometer can either calculate both thickness and refractive index of the layer or it can be given a fixed refractive index for which it calculates the respective thickness. I tested its accuracy with LPD-SiO₂ samples of a short growth time. The results show that the ellipsometer is quite inaccurate at giving the thickness or refractive index of layers thinner than about 30 Å, but does show the general trend of changing thickness in a series of samples. The test results are given in appendix A. When examining the trend, a fixed refractive index was used as for some of the thinner samples the calculated refractive index fluctuated randomly between 1.5 and 3. It is plausible that the refractive index in a series of samples would stay approximately the same.

To further explain differences between LPD-SiO₂ and LPD-ZrO₂, I made several precipitation tests by titrating H₂SiF₆ and H₂ZrF₆ with ammonia. As several of the substances corrode glass (mainly HF, which is a reaction product), it was not possible to use a digital pH meter for measurements. I therefore had to use traditional pH paper to measure most of the pH values. I estimate that the accuracy is generally about ±1. Also distinguishing very low pH values (1 and smaller) from each other was impossible.

In addition to the precipitation tests, I grew several samples in 25 wt-% H₂SiF₆ (2.2 mol/dm³, Acros Organics) saturated with SiO₂·xH₂O (Mallinckrodt Chemical) with only ammonia and water addition (route I). I have not seen any references to this in existing articles.

3 Results

3.1 Films grown

In most of the solutions, no actual growth was observed. In all cases, though, a constant-thickness layer was formed within one hour. The thickness can not be due to a measurement error, as almost all samples (with the notable exception of samples made by saturation type *iii*) were hydrophobic. Pure silicon is also hydrophobic, but even a native oxide makes it hydrophilic. Etching of the native oxide cannot be the case, because the samples were still hydrophobic even after several days, in which time a native oxide would have certainly been formed.

The presence of a layer is also shown by a gradual change in thickness as some growth parameter was changed, but when testing different lengths of deposition time, the layer thickness stayed approximately the same. It was noted, though, that most 1-2 hour samples were 10-20 Å thick, but almost all samples grown overnight (>16 hours) were approximately 50 Å thick. This might be caused by a gradual change in the growth solution, due to evaporation.

Table 1 presents the discovered trends. The exact results are left ambiguous on purpose, because the layers are so thin. All growth solutions had 10 ml of H₂ZrF₆ (7.6 mol/dm³ for types *i* and *ii*, 1.9 mol/dm³ for types *iii* and *iv*) and 5 to 10 ml of water. Increased temperature seemed to give a slight rise to the thickness, though no thorough study of this was made.

The H₃BO₃·xNH₃ solution was made by adding 25 wt-% (13.4 mol/dm³) ammonia to 0.5 mol/dm³ boric acid until the pH was 7 (measured with a digital pH meter). The boric acid - ammonia ratio was about 150:1. This is a bit surprising, because stoichiometrically the required amount of ammonia should be three times the amount of boric acid, giving a ratio of 9:1. This might be due to the extremely low acidity constant of boric acid, 5.4·10⁻¹⁰ for the first step and under 10⁻¹⁴ for the second [11, p. 8-43]. Therefore boric acid might not ionize

Sat. type	Variable parameter	Number of samples	Thickness Å	Trend*
<i>i</i>	$c(\text{H}_3\text{BO}_3) = 0.25 \dots 0.40 \text{ mol/dm}^3$	4	16...23	Down
<i>ii</i>	$c(\text{H}_3\text{BO}_3) = 0.00 \dots 0.10 \text{ mol/dm}^3$	5	13...20	Down
<i>ii</i>	Time = 1...6 h	5	9...16	None
<i>ii</i>	water amount = 50%...80%	4	9...16	Down
<i>ii</i>	$c(\text{H}_3\text{BO}_3 \cdot x\text{NH}_3) = 0.00 \dots 0.17 \text{ mol/dm}^3$	3	13...18	Down
<i>iii</i>	$c(\text{H}_3\text{BO}_3) = 0.00 \dots 0.09 \text{ mol/dm}^3$	4	~30...~50	None
<i>iv</i>	Time = 1...3 h	3	8...12	None

* as effect on thickness with increasing value of parameter.

Saturation types:

- i* Non-saturated $7.6 \text{ mol/dm}^3 \text{ H}_2\text{ZrF}_6$
- ii* Precipitate saturated $7.6 \text{ mol/dm}^3 \text{ H}_2\text{ZrF}_6$
- iii* Precipitate saturated $1.9 \text{ mol/dm}^3 \text{ H}_2\text{ZrF}_6$
- iv* Commercial SiO_2 saturated $1.9 \text{ mol/dm}^3 \text{ H}_2\text{ZrF}_6$

Table 1: Results of LPD- ZrO_2 with changing parameters. Only series with at least 3 samples are shown. The thicknesses are measured with a fixed refractive index of 2.00 and results are not expected to be totally reliable.

The only samples that grew over 25 Å (measured with refractive index of 2.00) in one hour, were the ones made with saturation type *iii*. Unfortunately, I did not have time to study them extensively. They were also the only samples that were hydrophilic after deposition. This is reasonable, as silicon dioxide is also hydrophilic (whereas HF-stripped silicon is hydrophobic). It is also the only solution to show some kind of growth pattern, though the samples were often too uneven to calculate a growth rate. Table 2 lists the obtained results for saturation type *iii* in full.

$c(\text{H}_2\text{ZrF}_6)$ mol/dm^3	$c(\text{H}_3\text{BO}_3)$ mol/dm^3	Time h	Refractive index	Thickness Å	Fixed $n=2.00$ thickness / Å
1.3	0	1	2.38	30...32	30...32
1.2	0.0063	1	1.33	37...65	26...46
1.0	0.021	1	1.63	53...69	26...62
0.86	0.086	1	1.23	55...68	33...37

0.95	0	1	1.40	52...125	45...85
0.95	0	2	1.45	103...110	86...89
0.90	0.0048	1	1.32	89...194	66...122
0.90	0.0048	18	1.18	710...839	283...301

The first four samples have 10 ml of H_2ZrF_6 and 5 ml of water and demonstrate the effect of boric acid addition.

The last four samples have 10 ml of H_2ZrF_6 and 10 ml of water and demonstrate the effect of deposition time.

Table 2: Results of LPD- ZrO_2 using 1.9 mol/dm^3 H_2ZrF_6 saturated with precipitate (saturation type *iii*).

3.2 Precipitation experiments

I titrated H_2SiF_6 and H_2ZrF_6 with 25 wt-% ammonia several times and obtained seemingly contradictory results. Figure 3 shows the titration curves. The filled bullets show the point where precipitation occurred.

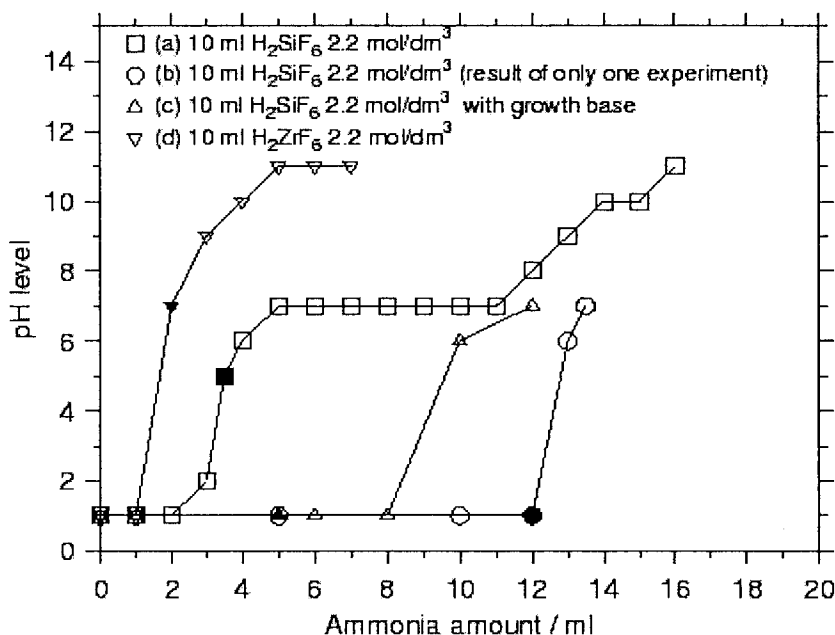


Figure 3: Titration curves of H_2SiF_6 and H_2ZrF_6 . Filled bullets mark the point where a non-soluble precipitate was formed. All pH values below 2 are treated as pH 1.

Curves (a) and (b) are totally contradictory, though both were done with same amounts of H_2SiF_6 and in a similar environment. Curve (a) is more common and easily reproducible. Curve (b) was obtained from only one experiment and I was not able to reproduce it. Curve (c) demonstrates the effect of adding a small amount of precipitate as a growth base after each ammonia addition. Curve (d) is the titration curve of H_2ZrF_6 .

The concentration of H_2SiF_6 and H_2ZrF_6 were both 2.2 mol/dm^3 . Addition of boric acid to H_2SiF_6 prior to titration caused the precipitate to form earlier, but otherwise the titration curve was like curve (a). When using 98 wt-% (7.6 mol/dm^3) H_2ZrF_6 or SiO_2 -saturated H_2SiF_6 , a precipitate formed with under 0.5 ml NH_3 addition.

It was also noted that the precipitate of H_2SiF_6 was insoluble in hydrochloric acid (HCl) when washed, but dissolved when HCl was added to the solution containing the precipitate. The precipitate from H_2ZrF_6 was soluble in high quantities (100-200 g/l) in HCl even when washed.

Figure 4 presents the thermogram of the precipitate.

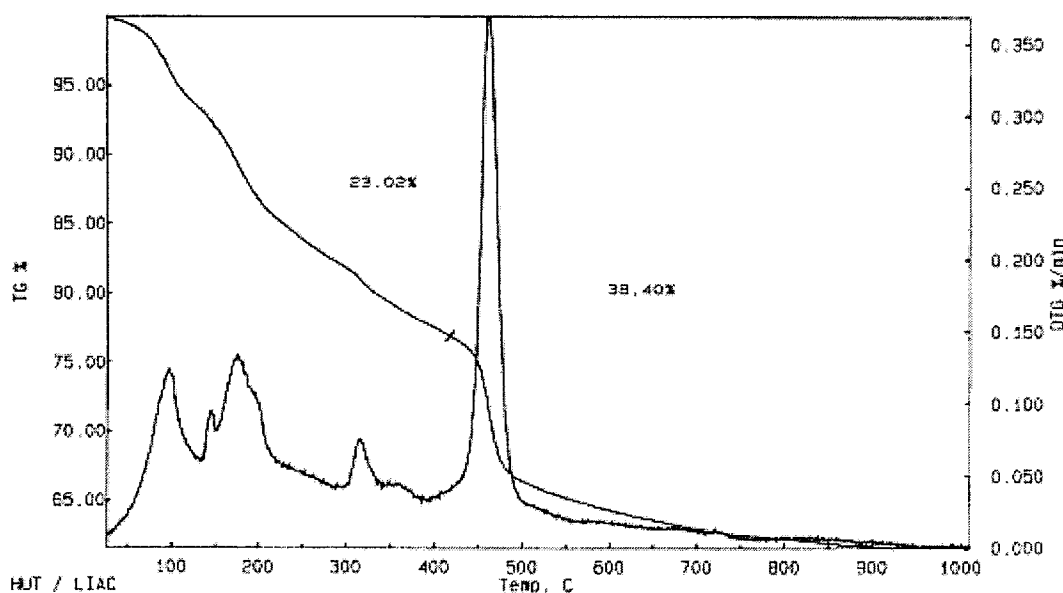


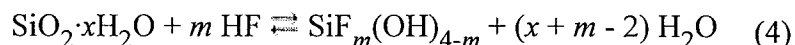
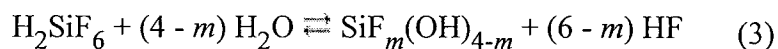
Figure 4: The thermogram of the precipitate

4 Discussion

The results show that direct substitution of Si with Zr is not totally sufficient in developing a process for zirconium oxide coating. Even though both have hexafluoro-complexes, they have subtle differences in other compounds. To understand the process better, it is necessary to further analyze the reactions in the LPD process.

4.1 Closer inspection of the LPD process

Chou and Lee [4] have proposed that an intermediate species $\text{SiF}_m(\text{OH})_{4-m}$ ($m < 4$) is formed in the reactions



with the first reaction occurring in the growth solution and the second one while saturating H_2SiF_6 . This intermediate species then reacts with the Si-OH bonds on the substrate surface forming a SiO_2 coating. This will not be further presented here, as it is not relevant in this study. For clarity, I present reaction (3) simplified with $m = 0$:



Substance	Exists only in solutions	Soluble in water	Soluble in acid	Soluble in HF

SiO ₂	No	No	No	Yes
ZrO ₂	No	No	Slightly	Yes
H ₄ SiO ₄	Yes	-	-	-
Zr(OH) ₄	No	No	Yes	-

Table 3: Solubility of silicon and zirconium compounds [11, pp. 4-83, 4-98].

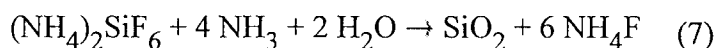
The solubilities of some of the substances involved are gathered in Table 3. It is notable that Si(OH)₄ (often written as H₄SiO₄, orthosilicic acid) exists only in solutions, while Zr(OH)₄ is an amorphous powder, insoluble in water. This casts doubt on whether the same reactions can take place with H₂ZrF₆.

Furthermore, SiO₂ is insoluble in acid (other than HF), but ZrO₂ is slightly soluble. This creates doubt whether zirconium oxide can be grown in an acidic environment, and at least limits the pH range and composition of the solution.

The growth with saturation type *iii* can be explained by Zr(OH)₄ dissolving into the acidic solution and then depositing either as Zr(OH)₄ or ZrO₂ onto the substrate. The exact composition of the layer deposited is unclear at the present time, though it is notable that the refractive index is much lower than that of a dense zirconium oxide layer (approximately 1.9 to 2.1). The reason why route I didn't function even with Zr(OH)₄ saturation might be the amount of Zr(OH)₄ that dissolved into the solution. The 98 wt-% solution might contain too much zirconium-compounds that not very much Zr(OH)₄ could dissolve. Diluting the solution reduces the concentration of these zirconium-compounds and enables more Zr(OH)₄ to dissolve. An important question for further studies is, does the solution have to contain any H₂ZrF₆ for deposition to occur.

4.2 Precipitation analysis

Reaction (3) can also be seen in some of the precipitation tests. The seemingly contradictory results can be explained by the high variety of reactions. The most common case, curve (a), precipitates at about 4 ml ammonia addition and thereafter the pH stays neutral until a bit over 10 ml. This is probably caused by the following reactions [12]:



First the ammonia reacts with H₂SiF₆ to form ammonium hexafluorosilicate ((NH₄)₂SiF₆). This consumes ammonia twice the amount of H₂SiF₆, stoichiometrically 3.3 ml. This solution is neutral, as both NH₄⁺ and SiF₆²⁻ have very low acidic constants. Then (NH₄)₂SiF₆ begins to react with the ammonia, creating a SiO₂ precipitate and ammonium fluoride. This consumes ammonia four times the amount of H₂SiF₆ or 6.6 ml. After this, all H₂SiF₆ has been consumed and the pH begins to rise slowly.

Curve (b) can be explained by reaction (5) proceeding to the right and ammonia consuming the resulting hydrofluoric acid. Thus the pH stays low until all H₂SiF₆ has been consumed. This is six times the amount of H₂SiF₆ or 9.9 ml. At some point some Si(OH)₄ (which can also be seen as SiO₂·2H₂O) dehydrates into forming

SiO_2 , giving a growth base for the rest of the $\text{Si}(\text{OH})_4$ to deposit to. This would also explain the trouble in reproducing the experiment, as there must not be any SiO_2 particles in the solution.

Curve (c) can be explained with the same reactions as (b), only the dehydration happening earlier, due to the growth base.

Curve (d) differs greatly from the other results. Precipitation occurs already at about 2 ml with a significant rise in pH. Addition of boric acid to the solution also changes the titration curve dramatically with precipitation and pH rise taking place at higher ammonia concentrations. Further study is needed to fully understand the exact reactions that happen in the solution, but this shows that the reactions of H_2ZrF_6 differ significantly from those of H_2SiF_6 . Addition of boric acid only increases the amount of possible reactions as it can either consume hydrofluoric acid or neutralize ammonia, both of which decrease the acidity but to a different degree.

The solubility tests support these findings. When hydrochloric acid is added to the solution, it consumes the ammonia, releasing hydrofluoric acid in which the SiO_2 precipitate dissolves. When the precipitate is washed, the ammonium fluoride is removed and the pure SiO_2 doesn't dissolve in the acid. The precipitate forming in the reaction between H_2ZrF_6 and ammonia is probably $\text{Zr}(\text{OH})_4$ or ZrO_2 , both of which dissolve in acid. The amount of precipitate that dissolves might suggest a high content of $\text{Zr}(\text{OH})_4$ as it dissolves more readily.

The thermogram (Figure 4) also suggests that the precipitate is $\text{Zr}(\text{OH})_4$. Assuming the beginning product is $\text{Zr}(\text{OH})_4$, the drop in weight for $\text{Zr}(\text{OH})_4 \rightarrow \text{ZrO}_2 + 2\text{H}_2\text{O}$ is 22.6 %, corresponding the drop from the beginning to the tick. The steep drop after the tick could be the reduction from zirconium (IV) oxide to zirconium (II) oxide. $\text{ZrO}_2 \rightarrow \text{ZrO} + \text{O}$ would result in a drop of 10.1 %, approximately the height of the drop. The rest is probably due to impurities from the production process. It is therefore probable that the precipitate is mostly (~90 wt-%) $\text{Zr}(\text{OH})_4$.

4.3 LPD- SiO_2 with ammonia addition

I made four experiments of LPD- SiO_2 with only ammonia addition. Table 4 shows the experimental parameters and results of these tests.

H_2SiF_6 ml	Saturated	H_2O ml	NH_3 ml	Time h	Refractive index	Thickness Å	Rate Å/h
10	No	0	2	1.0	2.52	15	15
-	-	-	-	-	1.12 *	45	45
10	No	0	3	1.5	1.12	308	205
10	Yes	9	1	1.5	1.12	371	247
10	Yes	10	0	1.5	1.44	99	66

* Results given also with fixed refractive index as floating refractive index differs so much from the other results. Both are considered unreliable, but trendsetting results.

Table 4: Experimental parameters and results of LPD- SiO_2 with ammonia addition. The first two experiments were done at 25°C and the last two at room temperature.

One can see that the growth rates with higher concentrations of ammonia are drastically higher than the ones with less ammonia. This indicates a higher concentration of $\text{SiF}_m(\text{OH})_{4-m}$ through reaction (3) with ammonia consuming the hydrofluoric acid, stressing the importance of the intermediate species. Ammonia addition also seems to radically lower the refractive index of the film. This might be due to water incorporating in the film. Further investigation of this effect is, however, beyond the scope of this study.

5 Conclusion

A process for deposition of zirconium oxide, analogous to the liquid phase deposition of silicon dioxide, was attempted. No continuous growth was observed when the growth solution had been saturated at 98 wt-% concentration or when saturated with commercial ZrO_2 . A notable film was only deposited when pre-diluted H_2ZrF_6 was saturated with $\text{Zr}(\text{OH})_4$, though the exact composition of the film requires further study. This could be done by means of IR-spectroscopy, etch-rate testing and X-ray diffraction (XRD).

Acknowledgements

I would like to thank Antti Niskanen for guidance and encouragement, Helsinki University of Technology Laboratory of Electron Physics for the opportunity to use their facilities during the course of this study and Dr. Tuula Leskelä of the Laboratory of Inorganic and Analytical Chemistry for the thermogravimetric analysis.

Appendices

A Test results of ellipsometer accuracy

To test the ellipsometer's accuracy, I made four short LPD- SiO_2 samples. First two longer depositions were made in a growth solution consisting of 60 ml of SiO_2 -saturated H_2SiF_6 (35 wt-%, Lancaster Synthesis), 90 ml of H_2O and 8 ml of H_3BO_3 (0.5 mol/dm^3). After that four short dips were done and finally one one-hour deposition was performed. From the longer depositions it is possible to calculate the growth rate quite accurately. As LPD on native-oxide coated silicon is not known to have any delay of deposition after immersion in the growth solution [2] and the growth rates of the long depositions are approximately equal, we can calculate the approximate thickness of the short LPD layers. Table 5 lists the results of the one hour depositions and Figure 5 shows the results for the short dips graphically.

Stage	Deposition time	Refractive index	Thickness Å	Deposition rate Å/h
Before	1 h	1.44	184	184

Before	1 h	1.46	181	181
After	1 h 12 min	1.44	227	189
Average		1.45		185

Table 5: Longer LPD-SiO₂ results for test of ellipsometer's accuracy

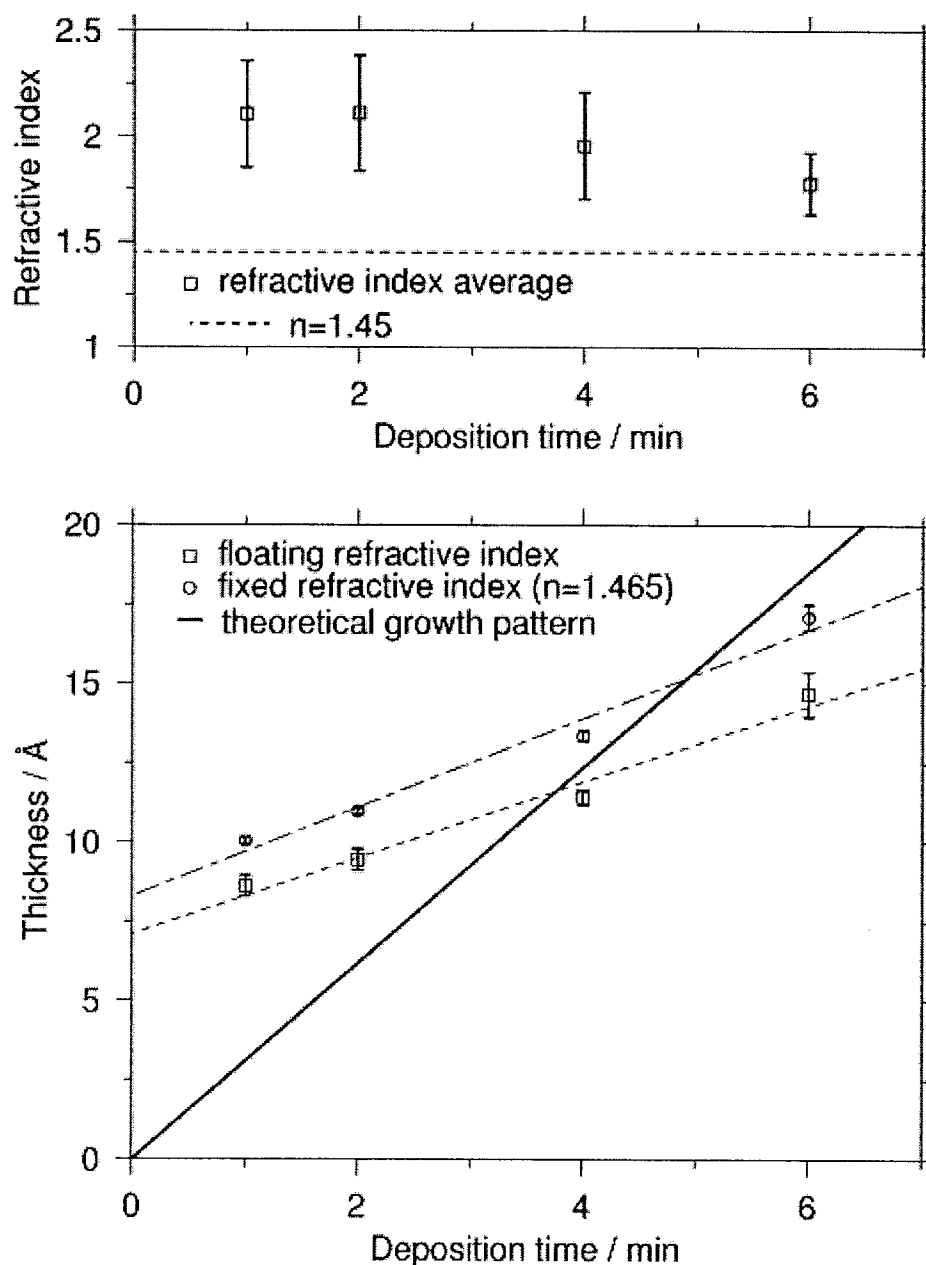


Figure 5: Thin LPD-SiO₂ results for test of ellipsometer's accuracy

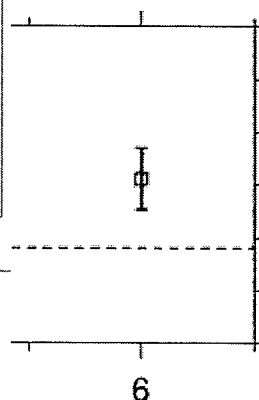
The ellipsometer is evidently not very accurate at measuring such thin films, but the results show a definite rise in thickness with growing deposition time. Thus, even for very thin samples the trend of thickness is shown. As expected, the measured growth rate between adjacent points also grows with time, approaching that of the theoretical growth rate. The results may therefore be quite unreliable below 30 Å, but already quite accurate over 50 Å.

B Molarity and percentage corres

Substance	Percentage	Molarity	Source
H ₂ SiF ₆	25 wt-%	2.2 mol/dm ³	Given density (1.27 g/cm ³)
	35 wt-%	3.3 mol/dm ³	From 25% correlance
H ₂ ZrF ₆	98 wt-%	7.6 mol/dm ³	Measured density (1.6 g/cm ³)
	35 wt-%	1.9 mol/dm ³	From 98% correlance
NH ₃	25 wt-%	13.4 mol/dm ³	Interpolated from [13]

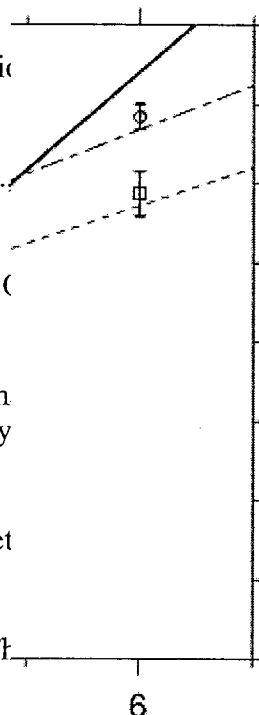
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Sampo Niskanen <sampo.niskanen at iki.fi>

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Exhibit B

Selective Electroless Metal Deposition for Integrated Circuit Fabrication

Chiu H. Ting* and M. Paunovic*¹

Intel Corporation, Components Research, Santa Clara, California 95052-8125

ABSTRACT

Selective electroless metal deposition process was studied for its applications in integrated circuit fabrication. Compared to selective metal deposition by CVD process, such as the selective tungsten deposition process, the selective electroless deposition process is more attractive due to its simplicity as well as process flexibility. A variety of material such as Ni, Co, Pd, and Cu were studied for contact filling, via filling, and for conductor patterns. These materials were selectively deposited on a variety of surfaces such as silicon, silicide, Al-Si, through patterned CVD silicon dioxide, CVD silicon oxynitride, and photoresist. Although this process is still in its early stage of development, very promising results have already been achieved. The experimental conditions and results for selectively filled contact holes, via holes, and conductor patterns are described using actual examples.

With the continued decrease in device dimensions and increase in scale of integration, modern VLSI (very large scale integration) chips often contain more than one million transistors. As a result, multiple layers of metallization are needed to provide interconnections for these devices. In the conventional IC fabrication process, these interconnection layers are fabricated by a series of physical vapor deposition or chemical vapor deposition (CVD) processes followed by photolithography and etching process for each layer. These repeated deposition and etching cycles are not only difficult and costly to perform, but they also generate severe surface topographies. Surface topography interferes with subsequent photolithography, deposition, and etching steps and is often the main cause of yield loss and reliability problems for VLSI chips. The topography problems are especially severe for contact holes (metal contact to silicon) and via holes (one metal layer to next), since they are not only small in dimension but also have high aspect ratios and nearly vertical sidewalls. There has been a great deal of effort in developing new fabrication processes that will give a more planar surface at contact and via levels. One very attractive approach is the selective

deposition of CVD tungsten into contact and via holes. The selective CVD tungsten process has been under intensive investigation for many years (1,2). It still has many technical issues, requires complex equipment, and is very costly. The selective electroless metal deposition is potentially a much simpler and less costly process in comparison to CVD W process. Even though the electroless deposition technology is used in the electronic industry, its applications have been mainly limited to printed circuit board fabrication and packaging of IC devices. It is the purpose of this paper to report the progress made in developing the electroless deposition technology for the fabrication of multilevel interconnections in VLSI circuits (3-5).

Deposition Processes

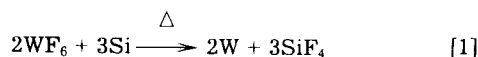
Electroless deposition occurs because of the driving force generated by chemical potentials at the depositing surface when it is in equilibrium with an ionic solution. Different materials establish different chemical potentials and selective deposition can be achieved when there is a significant difference in the chemical potentials between two surfaces. For example, the deposition process is highly favorable at chemically active surfaces such as silicon and aluminum against the chemically inert dielectric surfaces such as silicon dioxide or photoresist. The chemi-

*Electrochemical Society Active Member.

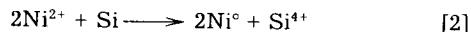
¹Present address: Physico Chemical Research, Inc., Port Washington, New York 11050.

cal reactions in the electroless process are quite similar to that of selective CVD tungsten deposition process. Since CVD tungsten deposition has been intensively studied, it is instructive to compare the reactions of selective electroless deposition to the selective CVD tungsten deposition on silicon surface.

When conditions are favorable, selective deposition on silicon can be achieved simply by replacing the surface Si atoms with the desired material. In the case of CVD W, the reaction can be expressed as

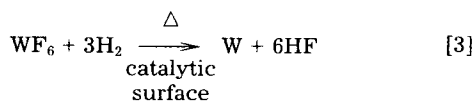


Since heat is needed for this reaction, the deposition process is carried out at elevated temperatures. The thickness of deposited W in this case is self-limiting since it needs exposed silicon surface to complete the reaction. The equivalent case for electroless Ni deposition can be expressed as

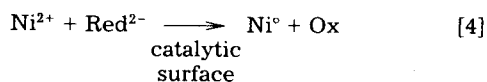


This reaction is commonly called displacement deposition since the nickel ions in the solution simply displace the silicon at surface. As in the CVD W case, the deposition thickness is also self-limiting. However, the reaction can be carried out in an aqueous solution and high temperature is not necessary.

In order to go beyond the self-limiting reaction given above, a reducing agent must be added. For selective CVD W, hydrogen is generally used (6), i.e.



Other than heat, the surface must be catalytic to this reaction. Since the original silicon surface and the deposited W surface are catalytic while silicon dioxide surface is not, selective W deposition can be achieved for contact hole filling. For electroless deposition chemical reducing agents, such as sodium hypophosphite, can be added to the solution to provide the electron needed for the following reaction



where Red is the reducing agent and Ox is the oxidized product of Red (6). Again, the surface must be catalytic to the reaction process. Since Si and deposited Ni surfaces are catalytic while SiO₂ surface is not, therefore contact holes can be selectively filled with Ni deposit.

Even though the above equations point to the similarities between selective CVD W and selective electroless Ni deposition process, there are important differences that make the electroless deposition process very attractive.

Table I. Composition of an electroless nickel deposition solution

NiSO ₄ · 6H ₂ O	40 g/liter
Sodium citrate	20 g/liter
Lactic acid	10 g/liter
DMAB	2 g/liter
NH ₄ OH	Adjust pH to 6.0

Besides the low reaction temperature, the electroless process has a wide choice of chemical reducing agents as well as a variety of activation processes which can modify the noncatalytic surfaces to become catalytic for subsequent selective deposition. Some examples of activation and deposition processes for IC fabrication are discussed below.

Contact Hole Filling

For integrated circuits, contact holes are patterned in a dielectric layer, such as phosphosilicates glass (PSG) or borophosphosilicate glass (BPSG). The Si surface in the contact holes can be either n⁺ or p⁺ doped. Recently silicides of Ti, W, and Co are often used in the contact region to improve device performance. In this work electroless nickel and palladium are studied for contact hole filling. The reasons for selecting Ni and Pd are due to the fact that a great deal of knowledge is available on the electroless deposition process of these materials (7, 8). Furthermore, both Ni and Pd have been used in the past to form ohmic contacts to silicon with good results (9).

Since the silicon surface is catalytic to Ni deposition, there is no need to activate the surface before deposition. A typical composition for an electroless Ni deposition solution is given in Table I. It contains NiSO₄ as the source of Ni ions and dimethylamineborane (DMAB) as a reducing agent. Although DMAB is specified as a reducing agent in Table I, we have also used sodium hypophosphite as a reducing agent. Nickel deposited with DMAB as a reducing agent is of higher purity as compared to that obtained with hypophosphite as reducing agent (7). Since the silicon surface is extremely smooth, a slight etch before the deposition helps to initiate the deposition process as well as to improve the adhesion of deposited Ni. The etching solution used is a mixture of HF and HNO₃. An example of Ni-filled contact holes is illustrated in Fig. 1. The contact holes in Fig. 1 have a nominal size of 1.5 μm and the CVD oxide thickness is approximately 1.0 μm. The filling is almost perfect except in this case the edge is slightly higher than the middle.

Silicided contact surface such as titanium silicide or tungsten silicide are not catalytic to Ni deposition, therefore, the surface must first be activated. Palladium is often used for surface activation (10-12). The composition of a typical Pd activation solution is given in Table II. The activation process can be accomplished by simply immersing the sample in the activation solution for a few seconds. The sample is then rinsed in DI water before Ni deposition.

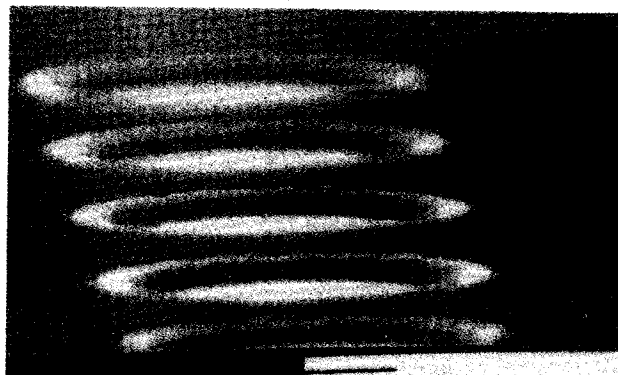
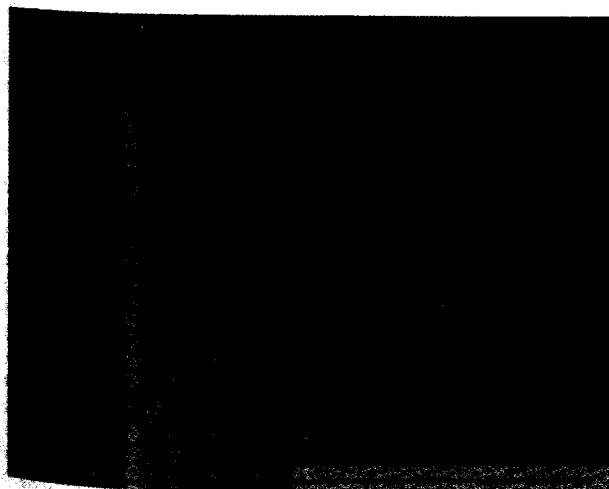


Fig. 1. Contact holes filled by Ni on Si surface. (a, left) Contact array, (b, right) enlarged view of filled 1.5 μm contact holes

Table II. Composition of a Pd activation solution

PdCl ₂	0.2g
HCl	1 ml
Glacial acetic acid	500 ml
HF (50:1)	250 ml
H ₂ O	245 ml

Since the silicides are catalytic to Pd deposition, the process can be simplified by using Pd directly to fill the contacts. This can be accomplished by using a Pd electroless deposition solution such as given in Table III. Very good fills have been obtained on a typical CMOS process with Ti silicide contacts. This is illustrated in Fig. 2. Figure 2a shows the Pd filled n⁺ and p⁺ silicon contacts (nominal 2 μ m size) as well as butting contact (large oval shaped contact when polysilicon layer overlaps into the contact hole) (13). Figure 2b shows the contacts to polysilicon layer on the same chip.

Although the contact holes on Fig. 1 and 2 are properly filled with Ni and Pd, there are many device-related issues such as mobile ion contamination, junction leakage, etc., which need to be examined. Furthermore, the thermal stability of the deposited material and its diffusion or silicide formation also need to be examined. A diffusion barrier layer between the deposited material and silicon device may be needed to reduce the above concerns and improve device reliability (13).

Via Hole Filling

For via hole filling, the deposition surface is Al (Al-1% Si) rather than silicon or silicide. Aluminum is not catalytic to Ni deposition, therefore an activation step is necessary. The Pd activation solution given in Table II can also be used to activate the Al surface for Ni deposition. However, the via filling process is, in general, more complex than the contact hole filling due to variations in Al surface conditions. Al surfaces oxidize easily, have various grain sizes, and form hillocks due to thermal stresses generated during the wafer fabrication process. Furthermore, Al is attacked by both highly acidic or highly alkaline solutions used in the activation and deposition processes. However, with proper care, uniform via fills can be achieved (14). This is illustrated in Fig. 3. Figure 3a shows an array of filled via holes at low magnification over the aluminum surface. The via holes are of 1.5 μ m nominal size etched in approximately 1 μ m of undoped CVD oxide. Aluminum hillocks can be seen in the background. Figure 3b is the SEM photograph of individual vias showing very good fillings.

Since Al surface is catalytic for Pd deposition, this process can be simplified by using Pd directly to fill via holes. Electroless Pd deposition solution such as that given in Table III, can be used to fill via holes also. The results are shown in Fig. 4. Figure 4a shows the filled via hole array while Fig. 4b is the SEM photo of individual via holes.

Table III. Composition of an electroless Pd deposition solution

PdCl ₂	1.4 g/liter
HCl	1.5 ml/liter
NH ₄ OH	200-400 ml/liter
NH ₄ Cl	5-10 g/liter
NaH ₂ PO ₂ H ₂ O	1.5 g/liter

Again, very good fillings can be obtained. Hydrazine was used as the reducing agent for the Pd deposition shown in Fig. 4. The reason hydrazine was selected for this study is because hydrazine can give very high purity in the deposited metal as compared to other reducing agents such as hypophosphite (7). However, hydrazine solution is corrosive to Al and is more difficult to use.

Materials other than Ni and Pd can also be used for via filling (14). A Co deposition process has also been developed for via filling. Again, a Pd activation step is necessary before Co can be deposited. When device contamination is not a problem Cu or Au can also be used to fill via holes. One such example is the fabrication of silicon substrates with multilevel interconnection. These substrates are used to integrate many chips into a single package to eliminate the performance limitations imposed by conventional single chip packages (15). Multiple layers of polyimide dielectric and Cu conductor lines are often used in these silicon interconnection substrates (16). For good electrical characteristics, the polyimide dielectric layer is usually rather thick ($\geq 5 \mu$ m). Via holes in the thick polyimide layer should be filled to achieve planar surfaces for subsequent processing. An example of filled via hole in polyimide is shown in Fig. 5 where selectively deposited electroless Cu is used to fill the via holes (5 μ m or larger) formed in 5 μ m thick polyimide.

Formation of Conductor Pattern

Selective electroless deposition can also be used to form conductor patterns. Conductor patterns can be formed by depositing through a suitable mask such as photoresist pattern, therefore, eliminating the need of metal etching. Metal patterning by etching is difficult, and it is often the limiting factor for further improvements in device density and yield. The potential of using selective metal deposition process to form conductor pattern can dramatically simplify the fabrication of multilevel interconnection. Several applications of selective electroless deposition have been investigated, and examples of this preliminary work are discussed as follows.

By using Pd activation and Ni deposition process similar to that used in contact and via holes filling process, nickel conductor patterns can be formed using photoresist pattern as a deposition mask. In this case, a thin aluminum layer is first deposited over SiO₂ surface to form an adhesive layer between nickel and SiO₂. Unwanted Al between Ni lines can be etched away after the deposition of nickel. Figure 6a shows the deposited Ni conductor pat-

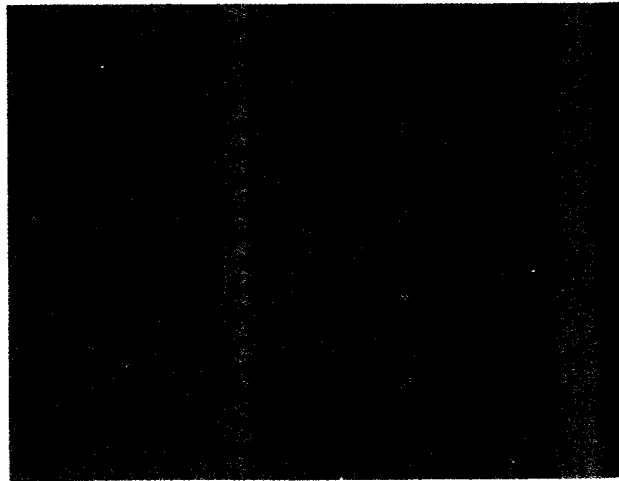
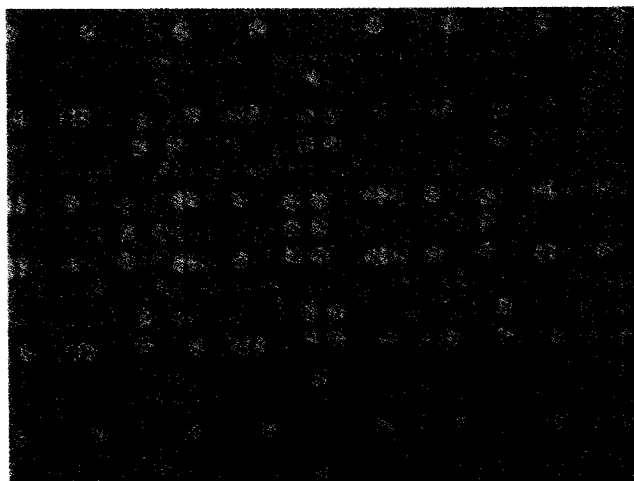


Fig. 2. Pd-filled titanium silicide contact holes on CMOS devices. (a, left) Contacts to n⁺ and p⁺ regions, (b, right) contacts to polysilicon regions

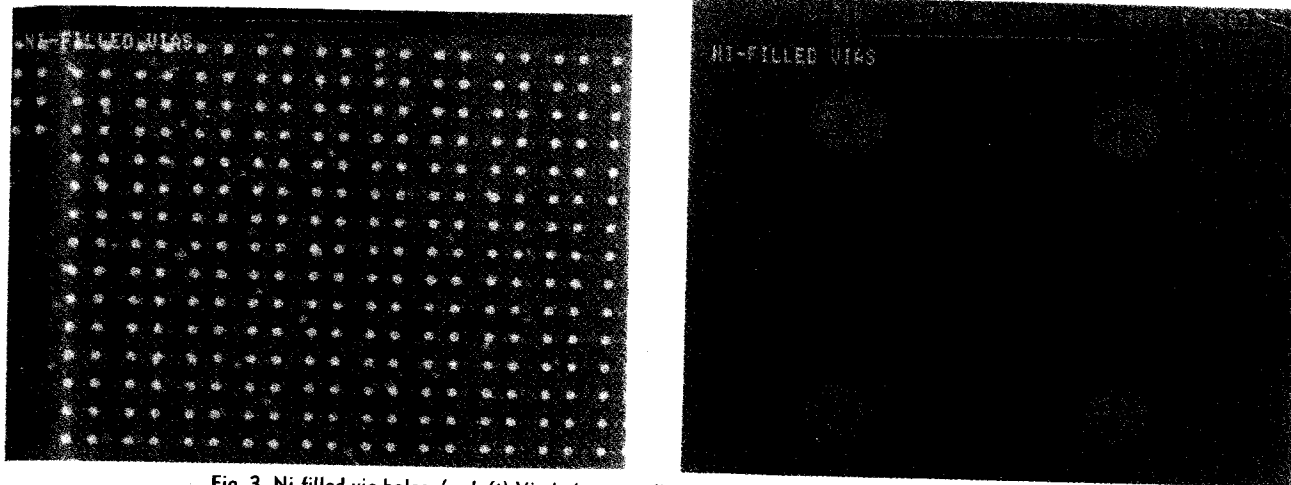


Fig. 3. Ni-filled via holes. (a, left) Via hole array, (b, right) SEM photo of the filled 1.5 μm via hole

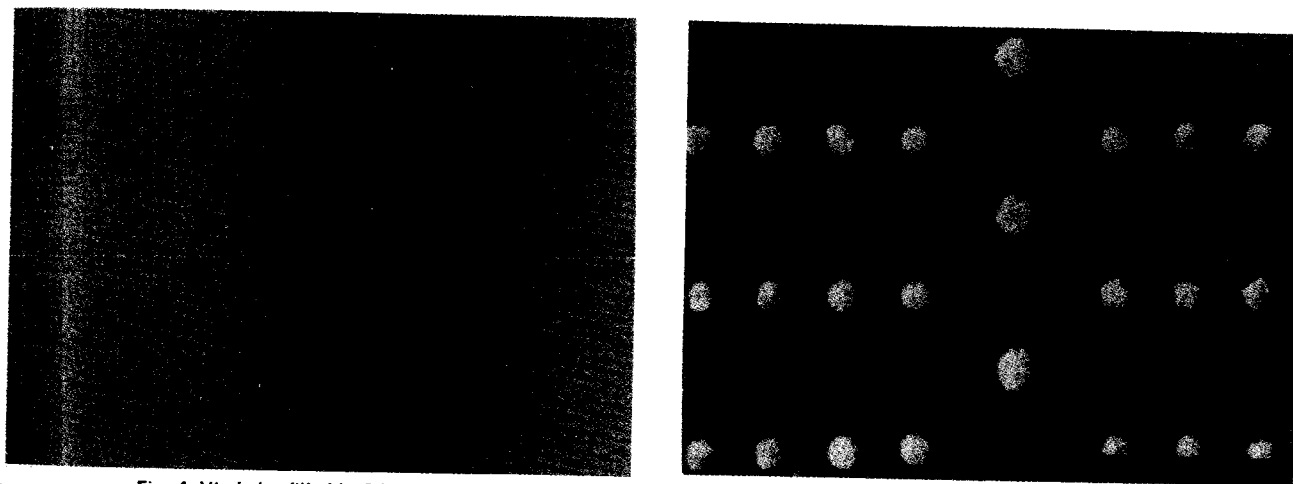


Fig. 4. Via holes filled by Pd on Al surface. (a, left) Via hole array, (b, right) SEM photo of the filled 1.5 μm via hole

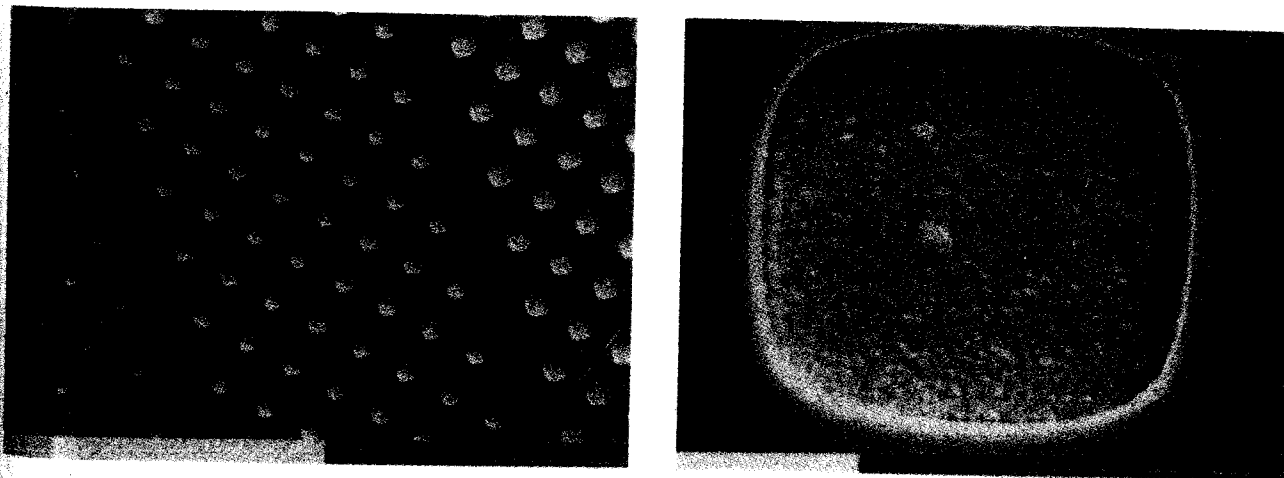


Fig. 5. Cu-filled via hole in 5 μm thick polyimide

tern after resist stripping. The minimum pitch of conductor pattern in Fig. 6a is 5 μm (i.e., line and spaces). The SEM cross section of the deposited nickel line is shown in Fig. 6b. It can be seen in Fig. 6b that the deposited nickel is over 1 μm thick with the edge somewhat thicker than the middle. It is interesting to note that the edge profile of the deposited nickel follows that of the resist contour which is slightly tapered. This is a demonstration of the high resolution capability of the selective deposition process. It can be used to generate metal patterns with resolution limited only by the photoresist process without any additional dimensional loss due to etching or resist erosion.

The selective deposition process can also be used to improve the metallization pattern formed by conventional

process. One such possibility is to overcoat or clad the aluminum lines with a more reliable material. Selective W was used to clad Al line with improved reliability (17). A better clad material may be a thin layer of Cu since Al-Cu alloy has been used to improve the current carrying capability (i.e., electromigration) and suppress hillock formation (18). Figure 7 illustrates that electroless Cu can be selectively deposited over the Al conductor. Figure 7a is the schematic diagram, and Fig. 7b is the SEM cross section of 1 μm thick Al line overcoated with approximately 0.2 μm Cu.

Besides Al, other materials can also be used as the base layer. For example, thin Ti layer can be used as the base layer for electroless Cu deposition. Unlike Al, which has a

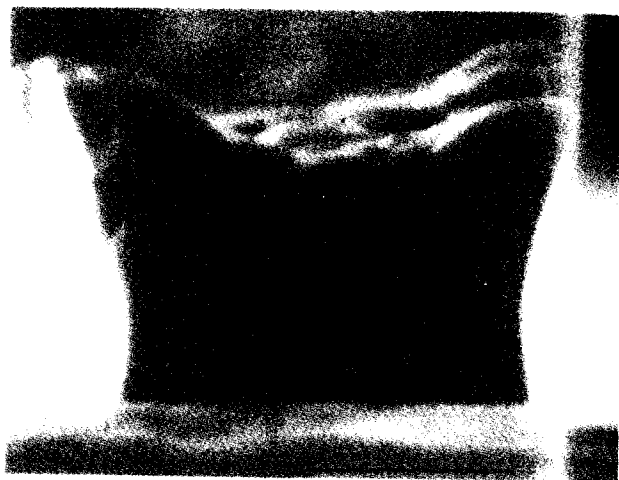
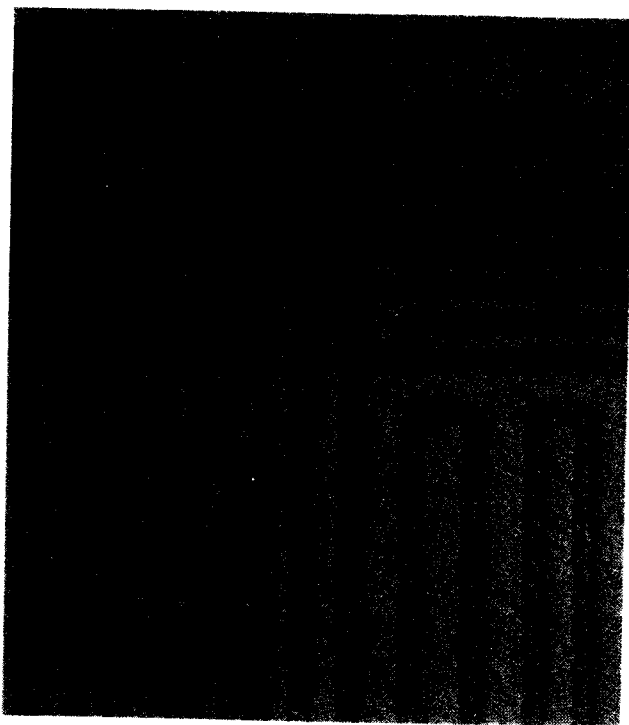


Fig. 6. Conductor pattern formed by depositing Ni through photoresist pattern. (a, left) Optical photo, (b, right) SEM cross section.

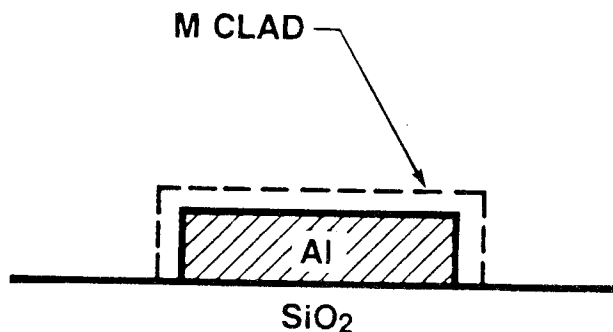
very large grain size, the thin Ti layer has a very smooth surface with very small grains. Therefore, Cu deposition on the Ti surface should be smoother and have smaller grains than the Cu deposition on Al surface (19). The SEM photo of electrolessly deposited Cu on Ti surface is illustrated in Fig. 8. It can be seen that the grain (crystallites) size of deposited Cu is less than $0.1\ \mu\text{m}$. Metal deposits of such fine grains (crystallites) are desirable for continued scaling of conductor line width.

Other than the planarization of contact holes and via holes, conductor pattern also needs to be planarized for the fabrication of multilevels of interconnection structures. Various etch back schemes, including simultaneous etching and deposition, have been used to achieve partial planarization of the dielectric layer over the conductor pattern. A better planarization scheme is to bury the metal pattern completely into the deposited dielectric layer so that the combined metal-dielectric layers will have a nearly ideal planar surface. By depositing metal selectively to fill an etched groove in the dielectric layer, a nearly ideal planar surface can be obtained. The proposed process is outlined schematically in Fig. 9 (20). First, a photoresist pattern is generated on the dielectric surface as in Fig. 9a, then the pattern is transferred to the dielectric layer by anisotropic etching process as in Fig. 9b. A base

metal for the selective electroless deposition, such as a thin Al (or Ti) layer, can be formed by the lift-off process (21) as illustrated in Fig. 9c and d. Electroless Cu is then selectively deposited to fill up the trench as in Fig. 9e. A spin-on dielectric layer such as spin-on glass (SOG) (22) can then be applied over the surface to give an almost perfectly planar surface as illustrated in Fig. 9f. The cross section of the completed structure is shown in Fig. 10 to illustrate that very good planarization can indeed be obtained (20).

Summary

Selective electroless deposition processes for Ni, Pd, and Cu have been developed. For catalytic surfaces the deposition can be carried out directly using either photoresist or CVD oxide as masks. For noncatalytic surfaces, an additional activation step is used to prepare the surface for selective deposition. Pd solutions are used to activate Al, Ti, and silicide surfaces for selective deposition. The feasibility for contact hole filling and via hole filling have been demonstrated. The selective electroless deposition can also be used to form conductor patterns without the need of an etching process. By depositing the conductor to fill an etched groove in the dielectric layer followed by a spin-on dielectric layer, nearly perfect planarization can be achieved.



CLADDING METALS Cu, Ni, Co

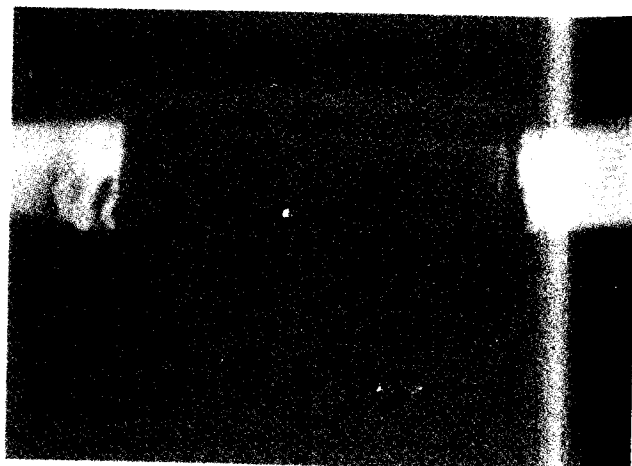


Fig. 7. Al line with Cu overcoat. (a, left) Schematic diagram, (b, right) SEM cross section.

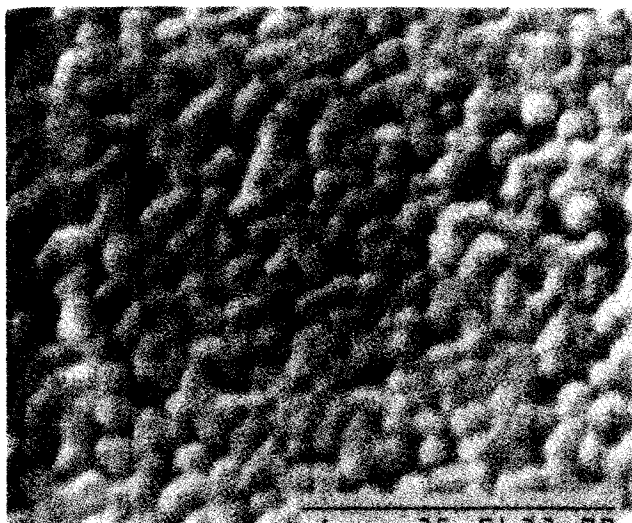


Fig. 8. Cu deposition over Ti surface

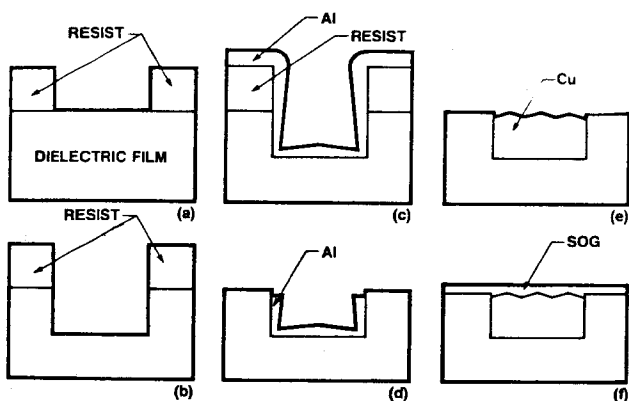


Fig. 9. Schematic of a buried conductor process: (a) photoresist pattern over dielectric, (b) pattern transfer by anisotropic etching, (c) deposition of thin Al layer, (d) base metal pattern formed by lift-off, (e) trench filled with electroless Cu, and, (f) a spin-on glass dielectric layer for planar surface.

Even though several examples have been discussed, there are possibly other variations as well as new applications which still need to be worked out. The versatility of the selective electroless deposition process can best be illustrated with a schematic diagram of a device cross section with two-level interconnections as shown in Fig. 11. Starting from silicon substrate there may be a contact barrier metal (CBM), a contact hole filling metal (CFM), and an adhesion metal layer (AM1) over the CVD dielectric followed by the first metallization layer (M_1). This process is then repeated for the second level interconnection starting possibly with a via barrier metal (VBM), a via hole filling metal (VFM), an adhesion metal layer (AM2) over the CVD dielectric followed by the second metallization layer (M_2). This process can be repeated again if more than two layers of interconnections are needed. Finally, after the bond pad opening in the passivation dielectric layer, there may be a bond barrier metal (BBM) and the bonding pad metal (BM) to connect it to the outside world by wire bonds, solder balls, or TAB (tape automated bonding). In Fig. 11, the optional layers are indicated by clear regions while the functional layers are indicated by cross-hatched regions. It is possible to use selective electroless deposition process to deposit all the functional layers indicated by cross-hatching.

Whether any or all the functional layers will be formed by selective electroless deposition process is not certain at the present time because there are no device yield and reliability data. However, selective electroless deposition represents a very attractive alternative to the conventional IC fabrication process. Some of these advantages and problems have been discussed here. A great deal of effort is still

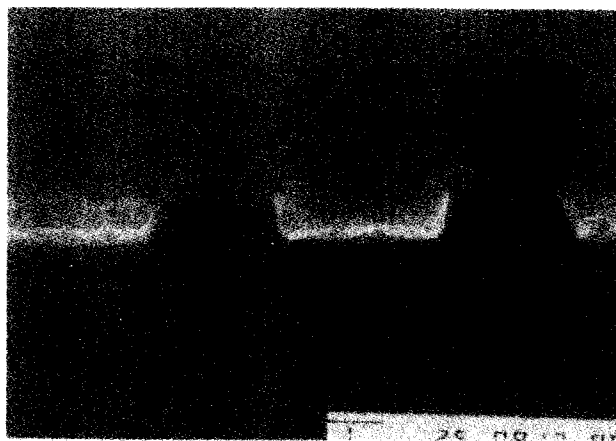


Fig. 10. Cross section for a buried Cu conductor line

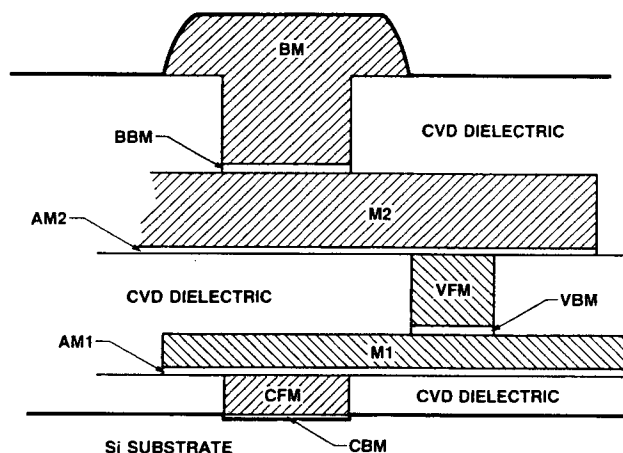


Fig. 11. Schematic diagram of a device with two-level interconnection structure.

needed to demonstrate material compatibility issues as well as manufacturability and device reliability issues.

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Selective Electroless Metal Deposition for Via Hole Filling in VLSI Multilevel Interconnection Structures

C. H. Ting,* M. Paunovic,*¹ P. L. Pai,* and G. Chiu

Intel Corporation, Components Research, Santa Clara, California 95052-8125

ABSTRACT

Selective electroless metal deposition process is investigated for via hole filling to provide a planar surface for the fabrication of high density multilevel interconnections. The substrates used in this work consisted of a 1.0 μm thick Al layer covered with 1.0-1.5 μm thick CVD silicon dioxide layer. Via holes of 1.5 μm nominal size are formed in the oxide layer by plasma etching. Selective deposition of Ni is achieved by first activating the Al surface in a Pd solution, Ni is then deposited on the activated surface from an aqueous solution using dimethylamineborane or hypophosphite as reducing agents. Pd can be selectively deposited directly on the Al surface without the need of surface activation. Either hypophosphite or hydrazine is used as the reducing agent in the Pd deposition solution. Cobalt can also be selectively deposited to fill the via holes. The filled via holes can have almost perfectly planar surface. Good contact resistance has been obtained by measuring the via chain resistance.

Multiple layers of conductors are needed to interconnect the large number of devices contained in a single VLSI (very large scale integration) chip. The surface topography created by multiple deposition and etching steps in fabricating the interconnection patterns presents a serious problem for subsequent processing. One of the most challenging issues is the step coverage at via holes because the via holes are not only small in size, but also have nearly vertical sidewalls. Therefore, a via hole filling process is indispensable to achieve a high density multilevel interconnection structure. Selective CVD (chemical vapor deposition) tungsten has been studied extensively for via hole filling (1). While much progress has been made, the selective CVD W process still has many issues. In this work, the selective electroless metal deposition process was studied for via hole filling (2, 3) as an alternative to the selective CVD W process. The selective electroless deposition process may provide an attractive alternative to the CVD process because it is a versatile, low temperature, and potentially very low cost process.

Experimental

Substrate preparation.—The substrates used in this study are thermally oxidized 100 mm diam silicon wafers. A 1.0 μm thick Al (with 1% Si) layer is deposited on the wafer surface by a conventional sputtering process. The Al layer is patterned with standard photolithography and plasma etching process. The minimum pitch of the metal pattern used in this work is 5 μm . A dielectric layer of 1.0-1.5 μm thick undoped oxide is deposited over Al by a low temperature CVD process (LTO). Via holes of 1.5 μm

nominal size are formed in the LTO layer using standard photolithography and plasma etching process. The photoresist is then stripped with either a solvent or by an oxygen plasma. These wafers are then used to study via hole filling using selective deposition of electroless Ni, Co, or Pd. For contact resistance measurements, a second Al-Si layer is deposited on the wafers after via filling. No special cleaning processes were used to clean the filled via surface before the second Al deposition. The second Al layer is then patterned using standard processes followed by a 450°C nitrogen anneal. The via chain resistance is determined by standard electrical measurements.

Palladium activation process.—Nickel is selected for via filling studies because there is a lot of information already available on electroless Ni deposition (4). Aluminum surface is, however, not catalytic to Ni deposition, therefore a surface activation step is necessary. Many different Pd solutions have been tested for Al surface activation (5, 6). The composition of a Pd activation solution that gives good selectivity between Al surface and oxide surface is given in Table I. The sample is first cleaned by dipping in diluted HF for a few seconds followed by DI water rinse. The sample is then immersed in the Pd activation solution for a few seconds and rinsed in DI water. Electroless Ni can then be selectively deposited on the activated Al surface without any deposition on the oxide surface. The excellent

Table I. Composition of a Pd activation solution

PdCl ₂	0.2g
HCl	1 ml
Glacial acetic acid	500 ml
HF (50:1)	250 ml
H ₂ O	245 ml

* Electrochemical Society Active Member.

¹Present address: Physico-Chemical Research, Inc., Port Washington, New York 11050.